Solvent-Free Iodination of Polyethylene via Twin-Screw Extrusion: A Scalable Approach

Emna Ben Ayed, Juliette Delcorps, and Olivier Coulembier*

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ABSTRACT: This study presents a novel, solvent-free approach for the iodination of polyethylene (PE) using twin-screw extrusion under mild conditions. The iodination process, typically challenging due to the inertness of PE, was successfully carried out using iodoform (CHI_3) as the iodine source and NaOH as the initiator, all at a low reaction temperature of 106 °C. Initial optimization using n-hexadecane as a model compound yielded efficient monoiodination, which was then extended to PE, achieving iodine incorporation levels of up to 23 wt %. The process was further applied to isotactic polypropylene (iPP), reaching iodine contents of approximately 22 wt %. The resulting iodinated polymers were characterized using ^1H NMR, SEC, FT-IR, TGA, and XPS, confirming successful iodine incorporation and the absence of polyolefin chain cleavages. Thermal analysis revealed significant changes in crystallinity and melting temperatures, directly correlated with the iodine content, especially for PE. This scalable, environmentally friendly method opens new avenues for polyolefin functionalization, enhancing their potential in advanced materials, including biomedical imaging and diagnostics, where iodine's high atomic number improves radiopacity, as well as flame-retardant polymers and polymers with improved coating and adhesion properties (Lex et al.et al. *Sci. Rep.* **2020**, *10*, 1508−8900; Kim *Elsevier* **2017**, 135−155).
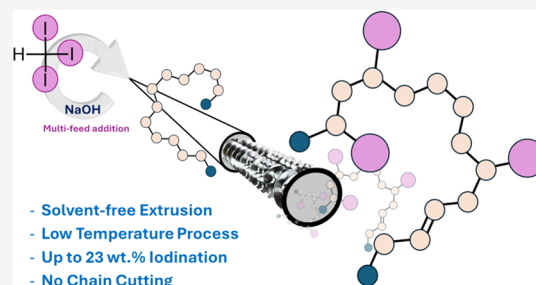
INTRODUCTION

The direct functionalization of unactivated C−H bonds in aliphatic hydrocarbons is a well-known concept that has remained a subject of continued relevance among the scientific community.[1−8] This growing curiosity and interest have led to substantial work on the transformations of the C−H bond, given its significant importance as the building block of the majority of nonmetallic materials, ranging from small molecules to long-chain macromolecules. Most synthetic activation strategies reported in the literature have utilized transition metal complexes,[9] metal carbenoids,[10,11] or catalysts[12] for amination,[13] hydroxylation,[14] azidation,[15] alkylation,[16] dehydrogenation,[17] and halogenation[18,19] reactions on low molecular weight compounds. In the early 2000s, Hartwig and Hillmayer[20] introduced the concept of C−H borylation[21] followed by the oxidation of a polyolefin using metallic complexes to achieve controlled, regioselective functionalization of polypropylenes. This breakthrough drew significant attention to the synthetic value of C−H activation chemistry in the field of materials.[22] These methods are undeniably appealing and diverse, with a strong capability to provide desired synthetic pathways for hydrocarbons. However, limitations such as scalability issues, harsh reaction conditions, sensitivity, and high costs of these metallic complexes or catalysts, along with their non-negligible impact on human health and the environment, cannot be disregarded.

Given these considerations, extensive research has been conducted to explore new, straightforward approaches that offer improved economic and environmental viability while maintaining or even enhancing the efficiency of existing methods.[23−25] Arguably, the most conventional metal-free method for the direct conversion of aliphatic C−H bonds in organic chemistry textbooks is the free radical process.[26] This approach has sparked significant research interest, leading to intensified efforts to expand its applicability to a variety of hydrocarbon molecules. Several studies have unveiled fascinating catalytic C−H transformations involving specialized precursors or catalysts to achieve desired products while avoiding hydrocracking, isomerization, or oligomerization of the target molecules.[22] For instance, Minisci et al. reported the catalytic monohalogenation of alkanes using N-hydroxyphthalimide (NHPI) as a precursor, which generates the phthalimido-N-oxyl (PINO) radical responsible for hydrogen abstraction from the alkane's C−H bond.[27] Similarly, another group used the same NHPI precursor and PINO radical for selective amination of aliphatic C−H bonds.[28] In 2014, Alexanian's group developed intermolecular C−H bromination[29] and chlorination[30] reactions by employing amidyl

radicals derived from *N*-haloamide reagents under visible light irradiation. This strategy has proven to be highly efficient due to the ability of nitrogen-centered radicals to achieve facile hydrogen atom transfer (HAT) across a broad spectrum of substrates, from small alkanes to complex molecules in late-stage synthesis.[31] Additionally, these halogenation reactions were conducted with the substrate as the limiting reagent, whereas traditional C−H functionalization approaches typically require a large excess of the starting material.[29,32] Building upon these remarkable characteristics, the same research group extended this protocol to C−H xanthylation in 2016.[33]

While the field of C−H diversification is rapidly expanding, certain C−H transformations, such as the iodination of aliphatic alkanes, remain highly restricted.[32] Iodine is considered as an excellent leaving group due to its large size and low electronegativity. Consequently, in nucleophilic substitution (S_N) reactions, iodine's ability to stabilize negative charge effectively and its weak bond with the carbon atom[34] make it highly desirable as a leaving group. However, due to the unfavorable thermodynamics associated with iodine itself (characterized by a large positive enthalpy of hydrogen abstraction),[35] only a limited number of articles have addressed the direct iodination of low-molecular-weight alkanes. Currently, most direct iodination methods rely on highly electrophilic entities such as perfluoroalkyl radicals,[36] *tert*-butyl hypoiodite (generated *in situ*),[37,38] or a combination of hypervalent iodine, I_2, and azoiodotrimethylsilane ($TMSN_3$).[39] While these strategies offer operational convenience for alkane iodination, they can be challenging and impractical due to the high instability of certain generated reagents[38] or the toxic and explosive nature of others.[40] To overcome these limitations, Schreiner et al. developed a promising phase transfer single electron (SET) approach utilizing crushed NaOH and iodoform (CHI_3) under mild conditions.[35] This method has been successfully applied to a wide range of strained aliphatic and poly(cyclic) hydrocarbons. In 2017, in collaboration with Schreiner, Artaryan et al. achieved the first iodination of hydrocarbons using an *N*-iodoamide at 100 °C under white LED irradiation.[34] However, while the iodination methods mentioned earlier exhibit a certain degree of diversity, they have primarily been restricted to small molecules. In contrast, other halogens or polar groups have been successfully incorporated into complex molecules and even polyolefins.[41]

Polyethylene (PE) is a low-cost commodity polymer extensively used in various applications, such as food storage, packaging, and biomedical devices.[2] However, its inert nature severely limits its interaction with polar additives, fillers, plastic blends, and materials like glass and metal.[36,37,42,43] To overcome these limitations and enhance the PE properties without compromising its performance, polar functional groups have been introduced along the polymer backbone.[44−46] This strategy has gained significant popularity due to its ability to greatly modify the physical properties of the final product, expanding its applicability in high-performance engineering applications. Numerous methods have been extensively developed and documented in several reviews, encompassing both metal and metal-free approaches.[41,47,48] However, since our focus aligns with metal-free radical approaches, examples in the literature have reported successful functionalization of PE while maintaining its properties. For instance, Zhou et al. achieved the first direct amination of PE using NHPI as an organic catalyst to cleave C−H bonds.[42] In

another study, the same group[43] introduced chlorine and bromine atoms into PE chains in a controlled manner using *N*-chloroamide[30] and *N*-bromoamide[29] reagents developed by Alexanian et al. Recently, regioselective functionalization of PE using the *N*-xanthylamide reagent under blue light exposure was reported.[49] Regarding iodinated PE, only a few reports have been published, relying on plasma technology where polymer films were exposed to iodine vapors for controlled durations.[47,48,50−52] XPS analysis indicated that after 141 days of exposure, an incorporation of 0.34 wt % iodine was achieved.[53] This finding suggests that iodination methods for PE as reported can be effective, but they necessitate significantly longer reaction times.

Here, we report for the first time the iodination of C−H bonds in PE under mechanochemical conditions (twin-screw extrusion) without organic solvents and under mild experimental conditions. Our initial studies on a linear alkane (*n*-hexadecane) revealed the highest conversion yields after optimizing the protocol suggested by Schreiner et al.,[35] in which we used iodoform as a cheap and stable iodine source and powdered NaOH as the initiator for the iodination reaction. The ratios of the reactants (alkane/CHI_3/NaOH), reaction duration, temperature, and shearing forces were carefully controlled to minimize any typical side reactions that could negatively affect the transformation of the alkane. We then extended this process to PE using a twin-screw extruder. Additionally, to a lesser extent, our conditions for iodination were successfully applied to polypropylene (PP). The workup of this reaction is a one-step process followed by purification and characterization of the functionalized polymer.

RESULTS AND DISCUSSION

Direct Iodination Using *n*-Hexadecane as a Small-Molecule Model. The combination of solid NaOH and iodoform powder has demonstrated efficient monohalogenation of cyclohexane, lightweight linear alkanes, and cyclic alkanes.[22,23,35,54,55] These transformations typically require the substrate to be used in large excess for optimal yield. High yields were achieved in these transformations, calculated relative to iodoform. However, these conditions are not suitable for iodinating polyolefins. To apply this transformation to a polymer, the reaction conditions, such as ratios, time, temperature, and shearing forces need then to be first optimized. Additionally, understanding the reaction mechanism and identifying potential side reactions that could cause cross-linking or degradation of polyolefins, such as polyethylene (PE), is crucial.

To determine the appropriate conditions for iodinating PE, several reactions were performed using *n*-hexadecane (*n*-C16) as a model compound. This choice was based on the characteristics of *n*-C16 as a long-chain hydrocarbon with only aliphatic C−H bonds, closely resembling the properties of PE. At first, the iodination reactions were conducted at 40 °C for 24 h using a combination of solid NaOH and iodoform (CHI_3). Experimental conditions mimicked those reported by Schreiner et al.[35] by using both *n*-C16 and the base in excess as compared to CHI_3 ($[n\text{-C16}]_0/[CHI_3]_0/[NaOH]_0 = 50/1/12.5$). ^{1}H NMR analysis in $CDCl_3$ revealed from the crude that the reaction predominantly produced monoiodinated *n*-C16, with iodination occurring selectively at secondary carbons ($\delta = 4−4.2$ ppm). The conversion yield, calculated relative to CHI_3, was approximately 1% (Table S1, entry 1). The analysis also showed the presence of unreacted starting material CHI_3 at $\delta =$
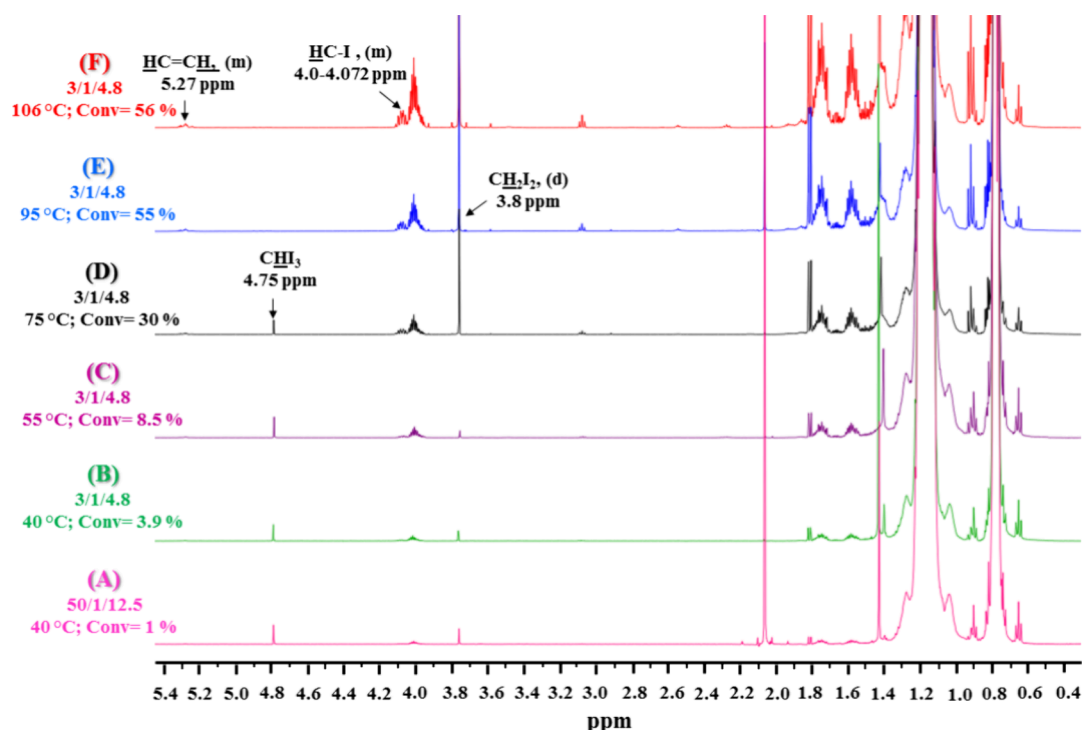
Figure 1. Conversions (conv. %) of *n*-hexadecane after iodination under varying $[n\text{-}C16]_0/[CHI_3]_0/[NaOH]_0$ ratios and reaction temperatures, supported by stacked ^{1}H NMR spectra (recorded in CDCl$_3$ at 21 °C).

4.89 ppm, and the formation of a side product, CH$_2$I$_2$, at δ = 3.86 ppm (see the Supporting Information, Figure S1).

This selection of reagents and conditions allowed us to evaluate the efficiency of NaOH and CHI$_3$ as a pair. At this stage, our primary aim was not to optimize conversion yields, but to justify the selection of these specific reagents (NaOH and CHI$_3$) for subsequent iodination reactions, acknowledging that adjustments could potentially affect overall conversions. While elemental iodine (I$_2$) and diiodomethane (CH$_2$I$_2$) did not yield iodoalkane, which was expected due to the endergonic nature of I$_2$ and the limited reactivity of CH$_2$I$_2$ as an iodine donor,[55] tetraiodomethane (CI$_4$) successfully facilitated the desired reaction, yielding approximately 1.6%, as confirmed by ^{1}H NMR analysis of the crude product (Figure S2 and Table S1, entry 2). During the reaction both CHI$_3$ and CI$_4$ coexist in equilibrium as 2 CHI$_3$ $\rightleftharpoons$ CH$_2$I$_2$ + CI$_4$, as previously reported.[35] Given its superior stability, safety benefits, and cost-effectiveness,[35] we chose to continue using iodoform (CHI$_3$) as the preferred reagent for our study.

In exploring alternative bases, we first evaluated various inorganic bases. Carbonate salts such as cesium carbonate (Cs$_2$CO$_3$) and potassium carbonate (K$_2$CO$_3$) were employed in the reaction (Table S1, entries 3 and 4). Although iodoalkane formation occurred, the conversion yields did not exceed 0.5%, which is significantly low. This low yield can be attributed to the reactivity of the ions released during the initiation stage of the iodination reaction, where hydroxide ions are more reactive than carbonate ones. By using potassium hydroxide (KOH), the reaction proceeded with a slight improvement in the conversion yield (Table S1, entry 5). This increase can be attributed to the greater reactivity of the base due to the larger ionic radius of K$^+$ compared to Na$^+$. KOH, however, is not practical for large-scale processes due to its higher cost and increased corrosiveness compared to NaOH. Organic bases such as 1,8-diazabicyclo[5.4.0]undec-7-

ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were also tested, but no formation of the iodoalkane was observed. Additionally, azobis(isobutyronitrile) (AIBN), a well-known radical initiator, was evaluated as a substitute for NaOH, but it did not result in the desired product. These findings indicate that the interactive coupling between CHI$_3$ and NaOH in this reaction system is not solely governed by basicity alone, suggesting that factors beyond the inherent basicity of the reagents play a crucial role. This observation underscores the complexity of the reaction mechanism, where considerations such as the specific reactivity of hydroxide ions and potential interactions between the reactants are pivotal.

As previously stated, while the combination of iodoform and NaOH has demonstrated effectiveness in the iodination of *n*-C16, the conversion yield of the desired product remains notably low. Our efforts were then directed toward optimizing the reactant ratios to enhance results. Additionally, the influence of temperature on the reaction was investigated to understand its impact on both the conversion and the possible generation of shorter chain products resulting from C−C bond cleavage or any side products other than the concomitant production of CH$_2$I$_2$. It is worth noting that to extrapolate our model study to the iodination of PE, the highest temperature investigated needs to be below the degradation temperature of the main CHI$_3$ reactant (T_d = 150 °C; Figure S3), should not exceed the melting point of the PE, and should ideally be close to the softening temperature of the PE chains ($T \leq$ 106 °C).[56] This balance ensures that the PE remains in a suitable state for reactive extrusion without becoming fully liquid.

Figure 1 presents stacked ^{1}H NMR spectra of the iodinated *n*-hexadecane crude product obtained under various temperature conditions and initial $[n\text{-}C16]_0/[CHI_3]_0/[NaOH]_0$ ratios. At 40 °C, increasing the concentration of the CHI$_3$/NaOH duo relative to the initial *n*-hexadecane content ($[n\text{-}C16]_0/[CHI_3]_0/[NaOH]_0$ = 50/1/12.5 < 3/1/4.8) enhances
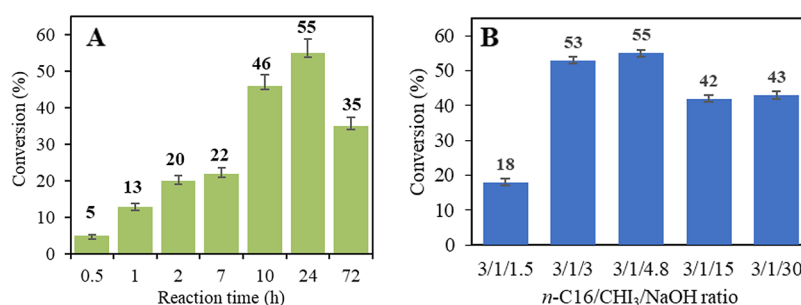
Figure 2. Iodination kinetics of n-hexadecane at 95 °C. (A) Influence of reaction time for an initial ratio of $[n\text{-C16}]_0/[CHI_3]_0/[NaOH]_0$ of 3/1/4.8; (B) influence of initial ratio of $[n\text{-C16}]_0/[CHI_3]_0/[NaOH]_0$ after 24 h.

the overall conversion from 1 to 4% (Figure 1A,B). Furthermore, maintaining the same ratio of components at 3/1/4.8 while increasing the temperature from 40 to 106 °C drastically enhances the conversion yield to 56% (Figure 1C−F). All spectra show no abnormalities or unrecognizable signals that could indicate the formation of smaller iodinated molecules resulting from C−C cleavages. However, under the specific experimental conditions employed, small compounds with low molecular weights or iodide salts (such as CI_4, C_2I_4, and C_2HI_5) could potentially be present in the resulting product and barely detected by ^1H NMR spectroscopy.[57] Prominent signals appearing at δ = 3.07 ppm (attributed to a proton adjacent to the iodine atom) and δ = 5.27 ppm (indicative of olefinic protons) suggest that iodination at this specific ratio and under elevated temperature conditions enhances efficiency. This also increases the potential for alkane polyhalogenation, which is a desirable outcome in our study.

Monitoring reaction time is crucial to prevent degradation, especially when applying this model to PE iodination. For instance, at 95 °C and with an initial $[n\text{-C16}]_0/[CHI_3]_0/[NaOH]_0$ ratio of 3/1/4.8, the iodination conversion increases with time, reaching a maximum of 55% after 24 h. After this peak, the conversion begins to decline due to the elimination of iodine atoms from the PE backbone, as evidenced by the appearance of olefinic protons in the ^1H NMR spectrum (Figure S4), as shown in Figure 2A.

Figure 2B explores the effect of NaOH concentration. A lower NaOH content (3/1/1.5) reduces the apparent conversion, while increasing the ratio to 3/1/3 or 3/1/4.8 maximizes it to 53−55%. Higher NaOH concentrations decrease yield again. The ^1H NMR spectra showed no notable differences, but the changing CHI_3/NaOH ratio impacts the distribution of active species (Figure S5). According to Schreiner et al., NaOH acts as a reducing agent, not a base, initiating the reaction by reducing *in situ* generated CI_4, forming triiodomethyl radicals ($^\bullet CI_3$).[35] These radicals abstract hydrogen from alkanes, forming CHI_3 and alkyl radicals. Alkyl radicals react with CI_4, producing iodinated alkanes and regenerating $^\bullet CI_3$, continuing the cycle (Scheme 1).[57−59]

Categorized as a phase transfer catalysis reaction, the mass transfer aspect significantly influences the overall conversion.[21,53] To investigate this, we studied the effect of system agitation speeds ranging from 0 to 400 rpm. Conversions were measured after 2 h of reaction at 95 °C with an initial ratio of $[n\text{-C16}]_0/[CHI_3]_0/[NaOH]_0$ of 3/1/4.8 (Figure 3). Without agitation, the conversion was low but increased with higher speeds, reaching up to 19%. However, excessively high agitation speeds and temperatures can cause the reaction

Scheme 1. Mechanism for the Iodination of Alkanes (R-H) Using Iodoform (CHI$_3$) and NaOH, Adapted from Schreiner et al.[35]
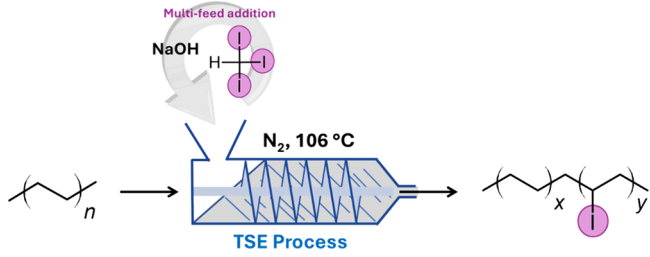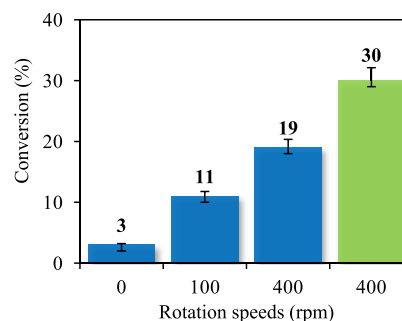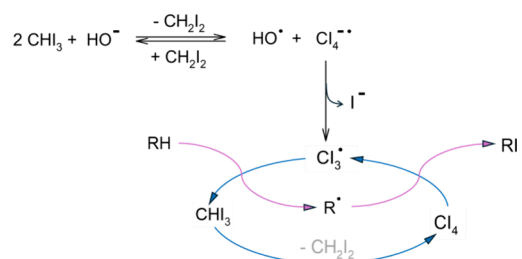

Figure 3. Overall impact of magnetic stirring speeds on the conversion of n-hexadecane at 95 °C ($[n\text{-C16}]_0/[CHI_3]_0/[NaOH]_0$ of 3/1/4.8) in a one-pot process (blue, one addition, reaction time = 2h) vs a multifeed process (green, four additions every 30 min).

mixture to adhere to the flask walls, impeding mass transfer and reducing conversion efficiency. Adding iodoform powder in portions every 30 min under constant stirring at 400 rpm significantly improved yields from 19 to 30% (Figure S6), demonstrating the effectiveness of this approach.

Direct Iodination of Polyethylene by Twin-Screw Reactive Extrusion. After optimizing the reaction conditions using a model light alkane molecule, a series of iodinated polyethylene (I-PE) samples were prepared using a twin-screw reactive extrusion (TSE) process. To the best of our knowledge, no previous studies have reported the iodination of PE in solvent-free conditions using a TSE process. In order to facilitate comprehensive molecular characterization, including ^1H NMR spectroscopy and size exclusion chromatography (SEC) analysis, we selected PE with a low molecular weight (theoretical molar mass, M_nth $\approx$ 1500 g/mol; M_wSEC = 7500 g/mol). This choice was crucial since higher molecular weight PE tends to be insoluble, limiting the range of analytical techniques that can be effectively applied. By using low molecular weight PE, we ensured that the iodinated samples

Table 1. Impact of Extrusion and Reaction Conditions on Polyethylene Iodination

								iodine wt %		
entry	sample code	$[ethylene]_0/[CHI_3]_0/[NaOH]_0$	reaction time (h)	SS (rpm)	M_wSEC(g/mol)	T_m (°C)	X_c (%)	XPS	^{1}H NMR	TGA
1	I-PE$_1$	3/1/1	2	100	9600	89.3	11.4		7	9
2	I-PE$_2$	2/1/1	2	100	12100	87.5	10.8		9	11
3	I-PE$_3$	1/1/1	2	100	15000	78.6	6			16
4	I-PE$_4$	1/1/1	2	200	13900	83.3	7	10	16	15
5	I-PE$_5$	1/1/1	2	300	12000	75	5			23
6	I-PE$_6$	1/1/1	1	100		87.4	6		13	9
7	I-PE$_7$	1/1/1	5	100		68	5			15

^{a}SS = screw speed. ^{b}Weight-average molecular mass as determined by SEC (THF as the eluent; 50 °C) with polystyrene standards for calibration. ^{c}Melting temperature and crystallinity percentage determined by DSC. ^{d}Melting temperature and crystallinity percentage determined by DSC.
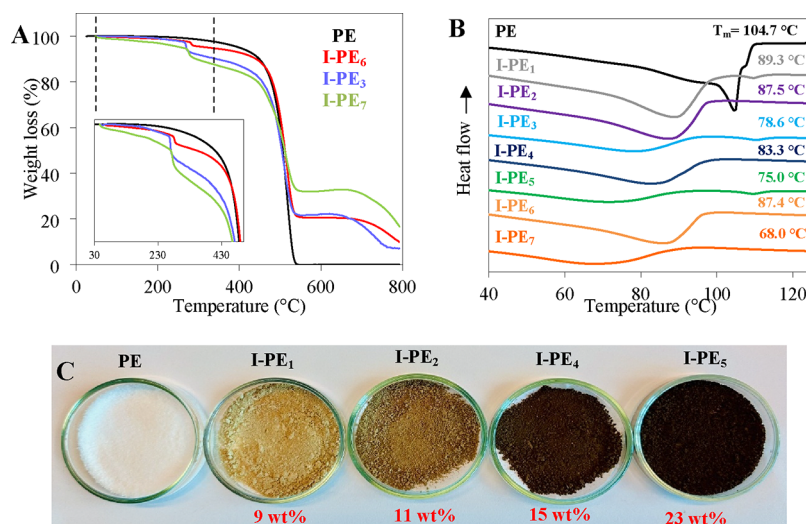
Figure 4. (A) TGA curves of the PE starting material and modified samples at different reaction durations; (B) DSC curves displaying the T_m of all the iodinated PE with all DSC data obtained from the second heating cycle at a rate of 10 °C/min; (C) digital photograph of selected iodinated samples.

remained soluble, thus allowing for a more detailed analysis of the reaction products and their structural attributes.

Although the initial conditions were optimized for a model alkane, these were adapted for the iodination of PE to better suit the polymer's characteristics. Based on findings with *n*-hexadecane, where an excess of NaOH relative to CHI$_3$ led to the generation of unsaturations due to the elimination of iodine atoms, a molar ratio of 1:1 for CHI$_3$/NaOH was selected for the PE iodination process. This choice was made to minimize the risk of unsaturation formation, as these reactions are inescapable but must be controlled. An excessive amount of NaOH could exacerbate the formation of unsaturations, potentially leading to unwanted radical-induced intermolecular cross-linking. Such cross-linking would be detrimental under extrusion conditions, as it could lower the polymer's decomposition temperature and alter its crystallinity. Additionally, an excess of NaOH could present experimental

challenges, such as difficulties in achieving uniform mixing and complications in process control during extrusion.

To avoid these risks, the quantity of NaOH was carefully limited, and for PE, only the effects of shearing force, *i.e.*, screw speed, and reaction time were systematically studied. The reaction conditions were meticulously controlled to maintain a 1:1 molar ratio between CHI$_3$ and NaOH. Results are presented based on the ratio $[ethylene]_0/[CHI_3]_0/[NaOH]_0$, with all reactions conducted under nitrogen at 106 °C using a multifeed addition method. In this approach, reagents were incrementally added every 30 min over a specific period of time. The detailed experimental conditions and results are provided in Table 1. Note, however, that in contrast to the iodination process of *n*-hexadecane, which involved simple physical filtration of the remaining starting materials, iodinated PEs were thoroughly washed and purified to remove excess iodoform powder (See Experimental Procedure, SI), ensuring the accuracy of the experimental results.
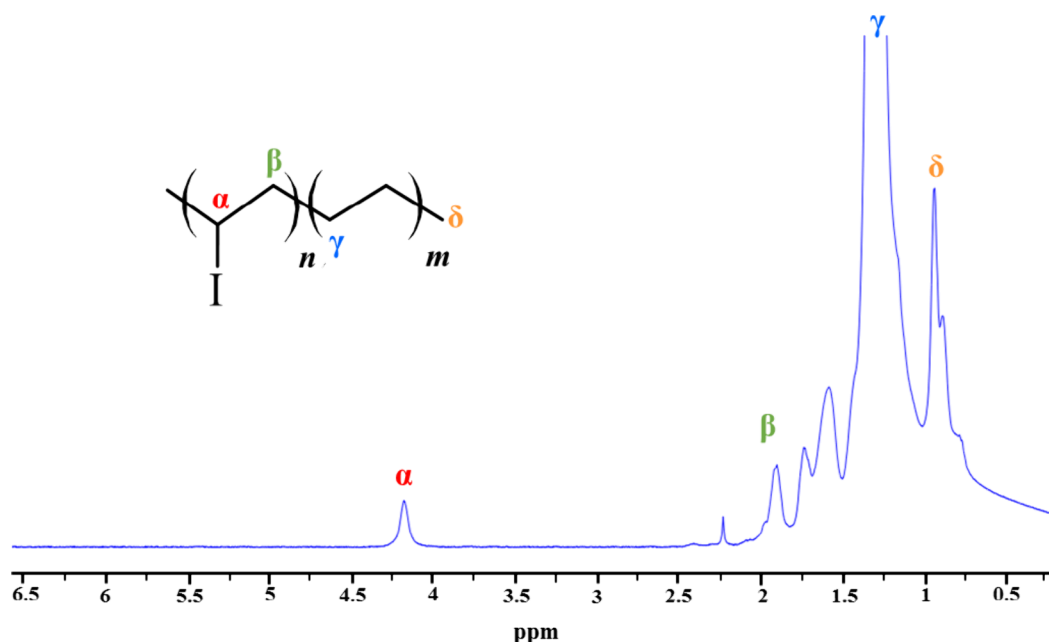
Figure 5. ^{1}H NMR spectrum of I-PE$_4$ in CDCl$_3$ solvent at room temperature (zoomed between $\delta = 0$ ppm and $\delta = 6.5$ ppm).

Our study began by adjusting the feed ratio of the ethylene unit to the CHI$_3$/NaOH duo (Table 1, entries 1−3) for 2 h at a screw speed of 100 rpm. By combining results from ^{1}H NMR and thermogravimetric analysis (TGA), we observed that the iodination weight percentages indicated a decrease in PE iodination levels when the $[CHI_3]_0/[NaOH]_0$ was reduced to the repeating ethylene units. This finding is consistent with the observations made for *n*-hexadecane. Therefore, to achieve a higher iodine content with minimal side reactions, we chose to maintain an equimolar ratio between the ethylene repeating unit, the haloform, and the base ($[Ethylene]_0/[CHI_3]_0/[NaOH]_0 = 1$) while varying the experimental conditions in each process cycle (Table 1, entries 3−7).

TGA is a valuable tool for evaluating how functional groups influence the polymer's thermal properties and can also provide estimates of the degree of halogenation in the samples. While ^{1}H NMR is typically a more precise method for assessing halogenation, the low solubility of our samples limited its application. Consequently, we have relied more on TGA for these evaluations. Typically, for halogenated polyolefins, the weight loss observed in the first stage can correlate with values obtained from more precise techniques.[43,60,61] Most TGA traces of iodinated polyethylene (I-PE) (Figure 4A and Figure S7) exhibit a three-stage degradation pattern, in contrast to pristine PE, which degrades in a single, smooth step starting at 350 °C and reaching zero mass at 530 °C. For I-PEs, the first degradation step begins around 250 °C, depending on the degree of functionalization corresponding to an elimination of HI gas, followed by significant decomposition between 400 and 550 °C, attributed to molecular scission and breakdown of the polymer's hydrocarbon skeleton. The final degradation stage starts at 650 °C, corresponding to the formation of cross-linked structures at higher temperatures. It is important to note that these cross-linking reactions are driven by the presence of carbon−carbon double bonds, whose quantity cannot be directly inferred from TGA analysis.

The iodine content in the functionalization process is strongly influenced by various parameters. For instance, higher shearing rates (I-PE$_5$) significantly increases iodine content compared to I-PE$_3$ and I-PE$_4$. This enhanced shearing promotes greater homogeneity and increases the polymer's active surface area relative to the halogenating reactant and the base. However, as the iodine content increases, the concurrent formation of double bonds intensifies, leading to cross-linking and the production of a more resistant material that becomes difficult to dissolve and characterize using techniques other than TGA.

Reaction time also proved to be a key factor in influencing the rate of functionalization. For example, after 1 h, the iodine content reaches 9 wt % (I-PE$_6$), while extending the reaction to 2 h nearly doubles the iodine content (I-PE$_3$, 16 wt %). Yet, longer reaction times did not improve the final outcome (I-PE$_7$, 15 wt %). Interestingly, the residual mass of I-PE$_7$ was higher than that of the other samples, suggesting that iodination eventually reaches a saturation point, and prolonged exposure to shearing forces may induce dehydrohalogenation, favoring the formation of additional carbon−carbon double bonds in the polymer structure, as evidenced by a pronounced and broad peak showing up at 1645−1569 cm^{-1} in the FT-IR data (Figure S8). This increase in iodination levels, along with the confirmed presence of carbon−carbon double bonds as shown by ^{1}H NMR and TGA, contributes to the noticeable darkening of the sample color. Both the higher iodine content and the presence of conjugated double bonds may play a role in this coloration. In contrast, I-PE samples with lower degrees of iodination exhibit colors ranging from yellow to light brown (Figure 4C). This color variation provides a visual indication of the degree of functionalization, with darker final products generally correlating with higher levels of both iodine and double bonds.

The melting temperature (T_m) of all modified samples was affected compared to the unfunctionalized PE, which has a T_m of 104.7 °C (Figure 4B). The reduction in T_m values is expected due to the incorporation of functional groups that act as defects within the crystalline regions, disrupting the crystallinity of the parent polymer, even at low iodine contents. Iodine, with a van der Waals radius of 1.98 Å, is a large, bulky functional group that can easily alter the crystallinity of PE. A

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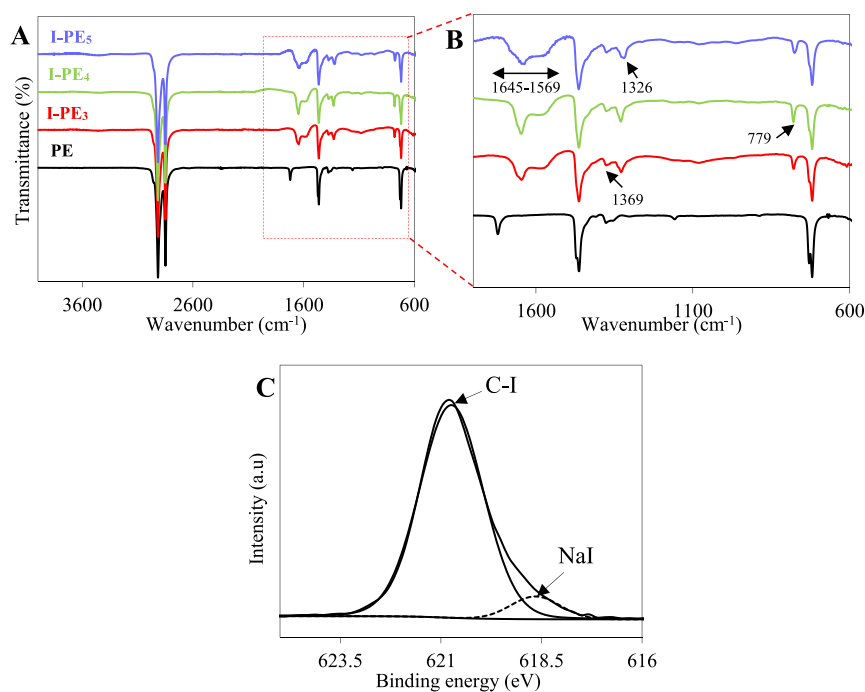
Figure 6. (A) FT-IR spectra of the PE starting material and iodinated PEs subjected to varying shearing rates; (B) Magnification of the 1800−600 cm^{-1} range to highlight key spectral features; (C) XPS spectrum showing the I 3d region of I-PE$_4$.

previous study by Plummer et al. demonstrated that the incorporation of halogens like chlorine and bromine into PE chains affects crystallinity, with bromine causing more pronounced changes due to its larger atomic radius compared to chlorine.[43]

In addition to the thermal analyses, ^{1}H NMR spectroscopy provided further insights into the structural modifications induced by iodination. I-PEs with an iodine content ≤15 wt % (Table 1, entries 1, 2, 4, and 6) exhibited good solubility in deuterated chloroform at 50 °C. The samples were analyzed promptly to prevent polymer recrystallization, showing an acceptable, though not perfect, correlation with the iodination weight content determined by TGA. Figure 5 illustrates the ^{1}H NMR spectrum of a selected iodinated PE sample (I-PE$_4$), used as an illustrative example to confirm functionalization. Compared to the unmodified PE (Figure S9), the spectrum reveals new chemical shifts: around δ = 4.11 ppm for α-hydrogens adjacent to the iodine atom and around δ = 1.7−1.9 ppm for β-hydrogens from neighboring −CH$_2$− units. These shifts are consistent with those observed in iodinated n-hexadecane, highlighting the changes induced by iodination on the polyolefin chain.

To complement these findings and to gain a deeper understanding of the structural changes, ATR-FTIR spectroscopy was employed. Figure 6A,B presents the results of the iodination reaction conducted at different shearing rates, ranging from 100 to 300 rpm (Table 1, entries 3−5). Visually, the intensity of PE's characteristic absorption peaks remained unchanged. However, an interesting observation was made regarding the doublet typically observed at 1470 and 720 cm^{-1}, which are associated with CH$_2$ bending and rocking deformation, respectively.[61] In I-PE sample, these doublets were merged into a single peak, indicating a modification in the crystalline packing of the polymer due to the incorporation of iodine atoms into the polymer backbone.[59] Furthermore, the intensity of the terminal groups, characterized by the CH$_3$

deformation peak at 1369 cm^{-1}, did not increase, suggesting that chain scission did not occur.[61] While the C−I stretching modes, usually found in the range of 600−200 cm^{-1}, were not visible with a germanium crystal,[62] new peaks appeared in the spectra of the modified samples. For example, the C−H deformation modes observed at 1326 cm^{-1} suggested alterations in the C−H environment around the polymer after modification.[63] A broad peak ranging from 1645 to 1569 cm^{-1}, assigned to C = C stretching modes, and a sharp peak at 779 cm^{-1}, corresponding to the = C−H bending mode of the cis conformation of an alkene, were also detected.[63] Typically, these stretching modes are found in the $trans$ isomer, which is characterized by an absorption peak around 970−960 cm^{-1}. The vinylene moiety was not detectable using ^{1}H NMR in the modified PEs, though it was present in the spectra of iodinated n-hexadecane with higher iodine content, albeit with variations in the ratio of double bond (0.4 mol %) to iodine content (23 mol %). The intensity and broadness of these peaks were notably heightened under conditions of increased shearing (I-PE$_5$) and extended durations of the iodination reaction (I-PE$_7$) (Figure S8). The final products exhibited high levels of cross-linking, rendering them very challenging to dissolve in any organic solvent. This observation suggests that cross-linking likely results from a combination of elevated iodine content and NaOH treatment, as NaOH induces olefinic sites in polyethylene, potentially leading to macroradical formation and cross-linking. While the exact mechanism remains under investigation, no evidence of oxidation of the double bonds was observed, as indicated by the absence of carbonyl groups characterized by an absorption band at 1710 cm^{-1} in all samples.[64]

X-ray photoelectron spectroscopy (XPS), while primarily a surface-sensitive technique, provided valuable elemental analysis, confirming iodine grafting onto the polymer chains. As shown in Figure 6C, the examination of the selected sample I-PE$_4$ revealed a new peak at 620.7 eV, attributed to chemically

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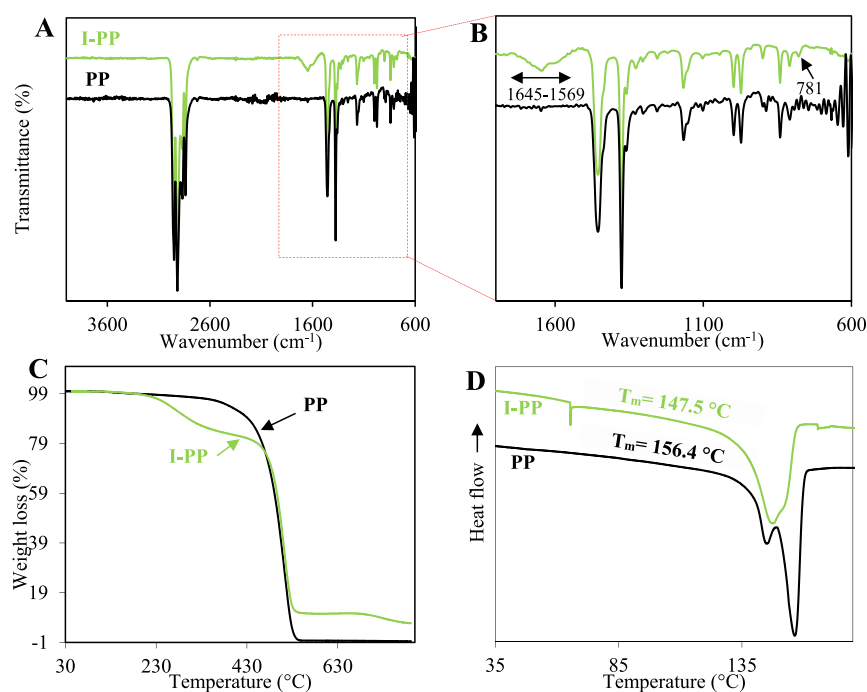
Figure 7. (A, B) FT-IR spectra of original PP and corresponding I-PP; (C) TGA curves of both iPP and I-PP; (D) second heating DSC curves of original iPP and I-PP (Exo up).

bonded iodine on carbon atoms.[47] Additionally, impurities from additives in PE and salts such as NaI, resulting from side products during the iodination reaction and/or purification, were identified. The C 1s spectra of the sample exhibited a strong, singular C−C absorption peak at 285 eV (Figure S10), with no splitting or emergence of new, lower intensity peaks within the same range, indicating a lack of complex structures.[65] The level of C sp^2 hybridization was not detected in the spectrum, suggesting that the vinylene moieties are internal or of very low amount, at least for I-PE$_4$. The iodine atomic percentage postmodification for 2 h using TSE was estimated at 1.72%, which corresponds to a mass percentage of 10 to 11% iodine in the polymer. Notably higher than the 0.34 wt % achieved after 141 days of exposure through I$_2$ plasma surface modification of polyethylene,[52] this iodine content is in agreement with the results obtained from ^{1}H NMR and TGA analyses, confirming the accuracy of the iodine content measurement.

Extrapolation to TSE-Based Polypropylene Iodination. The successful iodination of PE using TSE prompted us to consider applying a similar procedure to isotactic polypropylene (iPP), a widely used polyolefin feedstock appreciated for its high chemical resistance and exceptional mechanical properties.[62] Similar to PE, iPP consists of long C−H bonds with CH$_3$ pendants, rendering it more susceptible to degradation during functionalization, particularly under thermomechanical conditions. In the frame of our investigation, an iPP with a M_nth $\approx$ 5000 g/mol was selected. Literature extensively covers grafting reactions on PP in the melt state, particularly focusing on the grafting of polar synthons such as maleic anhydride, glycidyl methacrylate, and styrene. These reactions are typically initiated by free radicals generated from the thermal decomposition of organic peroxides, which preferentially attack the tertiary C−H bonds, leading to the β-scission, coupling, and isomerization side reactions.[63−65] To preserve the integrity of the parent

polymer during the iodination of PP, the same procedure as for the functionalization of PE was adopted ([Propylene]$_0$/[CHI$_3$]$_0$/[NaOH]$_0$ = 1, SS = 200 rpm), with the gradual addition of the CHI$_3$/NaOH duo over a 2-h cycle under nitrogen at 106 °C, a temperature close to the Vicat softening point of the polymer.[66,67] No solvents or additives were added during the process.

Although the final product was successfully collected and purified, its resistance to dissolution in organic solvents posed significant challenges for characterization. As a result, obtaining a complete ^{1}H NMR spectrum, or employing other techniques requiring solubility, was difficult. Nevertheless, we managed to conduct several tests on the collected iodinated PP (I-PP) using TGA, DSC, and FT-IR analyses.

The FT-IR analysis of I-PP reveals the same stretching, deformation, and rocking vibrations of CH$_3$ at 2953, 2873, 1377, 1156, and 971 cm^{-1}, as well as stretching and flexural vibrations of CH$_2$ at 2917, 2845, and 1459 cm^{-1}, found in the original iPP spectrum (Figure 7A).[68] A closer examination of the fingerprint region highlights the presence of internal C=C bonds, evidenced by a cis conformation (781 cm^{-1}) within the range of 1645−1569 cm^{-1} (Figure 7B). However, while these signals are present, they are less pronounced compared to those in the I-PE samples, even when comparing samples with identical iodine content. This suggests a lower degree of C=C bond formation in I-PP, indicating differences in the modification mechanism between PP and PE, despite similar levels of functionalization. This is confirmed by TGA analysis, which, in addition to a first 22 wt % dehalogenation step, observed between 230 and 450 °C, shows a charring percentage of 9 wt %, significantly lower than that observed in the analysis of I-PE samples (Figure 4A). Although the charring rate cannot be directly correlated to the percentage of carbon−carbon double bonds in a sample, a lower charring value suggests fewer C=C bonds, and thus fewer elimination reactions during the modification of PP.

Interestingly, the as-obtained I-PP exhibits a melting transition at 147.5 °C, which is slightly lower than that of the original iPP (T_m = 157.4 °C), while maintaining a relatively high degree of crystallinity (X_c = 23% for I-PP compared to 40% for iPP, Figure 7D). These results clearly indicate that modifying PP under these conditions is an effective approach to functionalize the polyolefin while preserving its crystalline structure and physical characteristics, which are valuable for various applications. However, further investigation is needed to fully understand the regioselectivity of the iodination reaction on PP, despite the successful modifications achieved.

■ CONCLUSIONS

We successfully demonstrate a novel and scalable solvent-free method for the iodination of polyethylene (PE) via twin-screw extrusion (TSE). Using iodoform (CHI_3) as an iodine source and NaOH as an initiator under mild conditions, iodine was efficiently incorporated into the PE chains, achieving up to 23 wt % iodine, while minimizing side reactions and polymer chain degradation. The iodinated polymers exhibited substantial changes in crystallinity and melting temperatures, directly correlated with iodine content, as confirmed by FT-IR, TGA, and NMR analyses. The application of this method to isotactic polypropylene (iPP) also yielded promising results, with iodine incorporation reaching 22 wt %. Furthermore, the results show that TSE-based iodination is not only environmentally friendly but also compatible with industrial-scale processes.

This work paves the way for new opportunities in the functionalization of polyolefins, enhancing their potential use in advanced material applications such as medical devices, packaging, and high-performance technologies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.4c03434.

> Experimental details of materials, general iodination procedures for n-hexadecane and polyolefins; complementary characterizations (TGA, ATR-FTIR, and ^{1}H NMR) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Olivier Coulembier − *Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers, University of Mons, Mons 7000, Belgium;* ⓞ orcid.org/0000-0001-5753-7851; Email: olivier.coulembier@umons.ac.be

Authors

Emna Ben Ayed − *Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers, University of Mons, Mons 7000, Belgium*

Juliette Delcorps − *Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers, University of Mons, Mons 7000, Belgium*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.iecr.4c03434

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■ ABBREVIATIONS

ATR	Attenuated Total Reflectance
FT-IR	Fourier Transform Infrared Spectroscopy
^{1}H NMR	Proton Nuclear Magnetic Resonance
I-PE	Iodinated Polyethylene
I-PP	Iodinated Polypropylene
M_nth	Theoretical molar mass
n-C16	n-hexadecane
SEC	Size Exclusion Chromatography
TSE	Twin Screw Reactive Extrusion

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