



Novel synthesis of branched polypropylene via solid-state shear pulverization



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ABSTRACT

As synthesized by Ziegler–Natta or metallocene catalysis, commercial polypropylene (PP) is linear and has low melt strength. A common approach for improving melt strength is to incorporate long-chain branches (LCBs). We describe the discovery of a novel approach to prepare LCB PP by subjecting linear PP to solid-state shear pulverization (SSSP) with benzoyl peroxide (BPO) as the lone additive. Depending on BPO content, LCB PP can be formed by radical reactions during SSSP or post-SSSP melt extrusion. Using shear rheology, we demonstrated that LCB PP was formed during SSSP of samples with 4 and 6 wt% BPO. Relative to linear PP, the post-SSSP sample (purified of residual BPO) made with 6 wt% BPO exhibited enhanced shear thinning behavior, a decreased dependence of storage modulus (G') on frequency (ω) at low ω , and a deviation from linear polymer behavior in its van Gurp–Palmen curve. For samples that were prepared with low levels of BPO (0.5–1.5 wt%), LCBs were not formed (within error) during SSSP; instead, LCBs were formed during post-SSSP melt extrusion (with residual BPO). While a sample with 1.5 wt% BPO showed no deviation from linear polymer behavior when tested immediately after SSSP, the same sample after post-SSSP melt extrusion demonstrated enhanced shear thinning behavior, decreased dependence of G' on ω at low ω , deviation from linear polymer behavior in its van Gurp–Palmen plot, and improved crystallization and tensile properties (as is expected for branched PP). We also showed that the LCB formation is achieved by taking advantage of the near-ambient temperature conditions associated with SSSP and is unattainable via conventional melt processing of PP.

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1. Introduction

Polypropylene (PP) accounts for almost 20% of plastics produced worldwide [1]. As well as being chemically resistant and easily processable, PP has a low cost of production allowing for its use in a wide variety of applications. Commercial production of PP is typically by Ziegler–Natta or metallocene catalysis, both of which lead to the formation of linear PP. However, linear PP has low melt strength and does not undergo strain hardening during extensional flow; this limits its utility in applications that result in deformation due to extensional flow, require high melt strength, or utilize processing conditions such as foaming, blow molding, film molding, or thermoforming [2–6]. Several techniques have been investigated as possible methods for producing PP with high melt strength; the

most commonly used (and studied) approach for improving PP melt strength is the incorporation of long-chain branches [2–8].

Long-chain branched (LCB) PP can be synthesized by direct polymerization [9–14] or post-polymerization processes such as ionizing irradiation [15–21], reactive extrusion using radical initiators [3,22–31], and reactive extrusion using previously functionalized PP [32–36]. Several studies have discussed the synthesis of LCB PP via polymerization reactions between propylene and macromonomers [9–11] or between propylene and dienes [12–14]. Challenges associated with such reactions include the possible cyclization of dienes [13], the need to use carefully selected iso-specific catalysts [14], and the need for additional synthesis and/or purification steps [9,10]. In an attempt to resolve problems associated with direct synthesis via polymerization, Ding et al. [12] studied the synthesis of LCB PP via a combination of ring-opening metathesis and acyclic diene metathesis polymerization. Although this method provided more control and utilized in-situ generated macromonomers, it was a complex multi-step process that required sophisticated monomers and specialized catalysts, thereby making scale-up processes challenging.

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Long-chain branched polypropylene has also been synthesized by post-polymerization ionizing irradiation [15–21]. Linear PP chains are irradiated with electron beams [17–19] or gamma rays [20,21] that have energies sufficiently high to cause the polymer chains to undergo scission resulting in the formation of PP macroradicals. In general, PP samples are first irradiated in an inert environment, annealed at elevated temperature (e.g., 80 °C [17–19]) to allow for radical reactions to occur, and annealed again at yet higher temperature (e.g., 130 °C [17–19]) to deactivate the radicals. During annealing, PP macroradicals participate in reactions such as branching, cross-linking, and degradation via β -scission. β -scission is a highly temperature dependent reaction that occurs as a result of rearrangement of a PP macroradical leading to the formation of two shorter chains, one with a terminal double bond and the other with a terminal radical [4]. In order to suppress the extent of chain scission, irradiation is carried out in inert environments and modified to include multi-functional monomers that stabilize PP macroradicals [18–20]. The major drawback of branching by irradiation is the presence of undesirable side reactions (cross-linking and chain scission) that lead to molecular weight (MW) reduction and hinder the synthesis of LCB PP with uniform and well-defined chain topologies [16–18]. Regardless of its challenges, branching by irradiation remains a major approach for commercial synthesis of LCB PP [3,4].

Alternatively, LCB PP can be synthesized by single-step post-polymerization melt extrusion of PP above its melt temperature in the presence of a radical initiator, with or without a multi-functional monomer [22–31]. During extrusion, radicals from the initiator abstract hydrogen atoms from the PP backbone to form PP macroradicals. For processes that use a multi-functional monomer [22–24], the macroradical then adds on to one of the double or triple bonds on the multi-functional monomer, leaving the other double or triple bond(s) free to attach to a macroradical on a separate PP chain. Thus, the multi-functional monomers serve as linkages between two or more PP chains leading to the formation of branched PP. However, due to high extrusion temperatures, synthesis of branched PP by this approach is accompanied by undesirable β -scission, which leads to MW degradation and hinders formation of well-defined, uniform chain structures [22,24]. There is also a concern regarding homopolymerization of the functional monomer during the grafting process [25,26]. In order to suppress β -scission and/or homopolymerization of functional monomer, additives such as iniferter compounds [22,27] and heteroaromatic ring derivatives [25] have been used. Su and Huang [28] also showed that use of supercritical carbon dioxide as a processing aid can reduce MW degradation that accompanies PP branching using a radical initiator.

We note that some crosslinking has been reported under conditions of high peroxide initiator concentration, relatively effective dispersion of initiator in PP, and high temperature near or in the melt state of PP [37–40]. Because β -scission is a first-order reaction while radical–radical reaction, which is essential for crosslinking, is a second-order reaction, higher crosslinking is expected at high macroradical concentration. In turn, high macroradical concentration is favored by high initiator loading and fast initiator breakdown. Chodák and Lazár [37] studied PP crosslinking achieved with different types of radical initiators, including benzoyl peroxide (BPO). Fast breakdown occurs with BPO near the melt temperature of PP (the half-life of BPO is on the order of 1 s at 170 °C [37,41]) when all initiator decomposition is spontaneous and even shorter in the presence of induced decomposition [42]). Although extremely high gel yield is not achievable with BPO because of induced decomposition at high BPO concentration, Chodák and Lazár [37] reported ~40% gel yield when a PP/BPO mixture with ~10 wt% BPO content was activated at 170 °C [37].

Gotsis and coworkers [3,29–31] studied the synthesis of LCB PP via melt extrusion in an inert environment with peroxydicarbonates (PODICs). Using a variety of PODICs, they observed that the extent of branching depended on the amount and molecular structure of PODIC added: PODICs with non-linear and bulky linear alkyl groups (which produced relatively stable radicals after decomposition) led to higher degrees of PP branching [29]. They postulated that addition of alkyl carbonate groups to PP could lead to reactions that were responsible for the formation branches during melt extrusion [29]. Branched PP prepared using PODICs has been shown to strain harden under extensional flow [29–31] and increase melt strength [29,31], extrudate swell [29], and processability in foaming and thermoforming [3]. The formation of LCB PP by melt extrusion with PODICs is a major approach to commercial production of high melt strength PP [43–45]. Nonetheless, as with other methods that rely on radical chemistries, LCB PP synthesis with PODICs results in non-uniform chain structure and is accompanied by MW reduction as a result of β -scission and the high processing temperatures that are utilized.

In an attempt to obtain uniform chain architecture and suppress β -scission, LCB PP has been synthesized by reacting functionalized PP with multifunctional monomers [32–36]. Examples include the imidization between maleic anhydride grafted PP (PP-g-MA) and ethylenediamine (EDA) [32,33] and the reaction between PP-g-MA and glycerol [36], both achieved by melt processing at ~180 °C. Lu and Chung [34] also prepared branched PP with comb structures by reacting PP-g-MA with amine group terminated PP in xylene at 130 °C for 5 h. Because these methods neither use radical initiators nor depend on radical chemistries, they are less susceptible to β -scission [35]. Using functionalized PP of well-known structure also allows for greater control over the LCB PP chain structures [34,35]. However, there remains the need to separately synthesize the functionalized PP before the synthesis of LCB PP, making these approaches multi-step processes [34,35] which are less attractive for commercial-scale production of LCB PP [32–36].

Here, we present the discovery of a novel method to synthesize LCB PP: solid-state shear pulverization (SSSP) of PP with a symmetric organic peroxide, BPO, as the sole additive. The SSSP process uses a twin-screw melt extruder modified with a cooling system to maintain the polymer in the solid state [46–59]. This process is accompanied by high shear stresses and compressional forces that cause repeated fragmentation and fusion of material; conditions are tuned by feed rate, screw speed, screw design, and temperature [46]. In addition to being solventless, SSSP is industrially scalable; polyolefins have been processed using a commercial-scale SSSP apparatus at rates exceeding 150 kg/hr. Compatibilization and intimate mixing of immiscible blends [47–51] and effective dispersion and exfoliation of filler in composites and nanocomposites can result from SSSP [52–55,58–61]. Recently, we showed that SSSP can be used to synthesize maleic anhydride grafted PP with strongly suppressed MW reduction [56] and ester functionalized PP with moderate MW reduction using a symmetric organic peroxide alone [57]. In the current study, we show that by taking advantage of the near-ambient temperature conditions associated with SSSP, LCB PP can be synthesized during SSSP or in post-SSSP melt extrusion.

2. Experimental

2.1. Materials

Polypropylene (Total Petrochemicals; MFI = 1.5 g/10 min; ASTM standard D-1238 at 230 °C/2160 g load; reported by the supplier) was used as received. Benzoyl peroxide and xylene were used as

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