Chapter

Introductory Chapter: Polypropylene - Synthesis and Functionalization

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1. Introduction

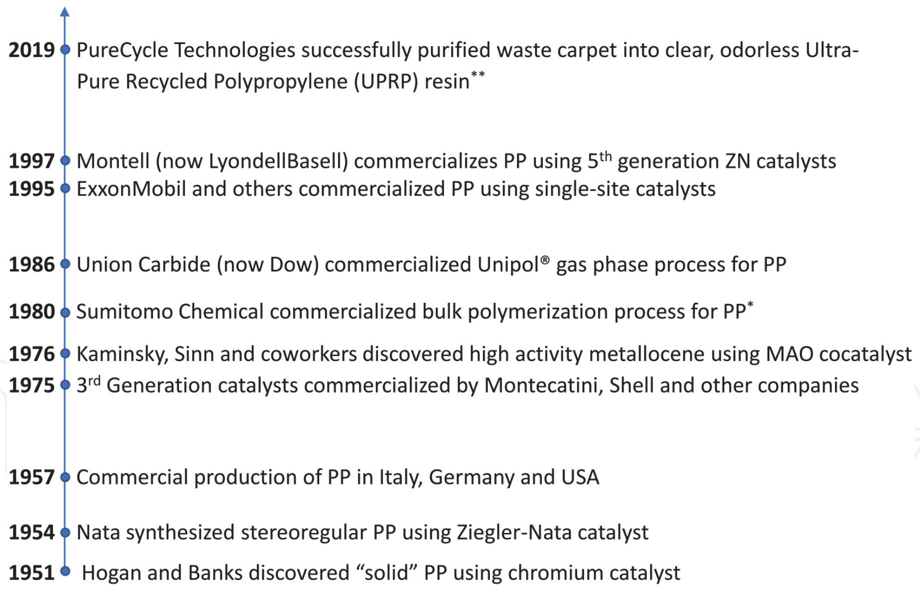
First discovered by J. Paul Hogan and Robert L. Banks in 1951, polypropylene (PP) is polymerized from propylene out of crude oil and is the most widely used commodity thermoplastic by volume [1]. Over the past 70 years, significant progress has been achieved to manufacture and commercialize PP (**Figure 1**) [2, 3]. The most recent milestone in the field of polypropylene is from PureCycle Technology, where the waste carpet has been successfully purified into clear, odorless ultrapure recycled polypropylene (UPRP) resin [4]. Through not fully commercialized yet, the innovation opens up a new venue of recycling processed PP into raw materials as a resin.

As one of the cheapest plastics with great processability, chemical resistance, and moisture barriers, PP with different tacticity found various downstream applications in textile, automotive, cosmetics, and consumer packaging. In 2016, 26% of polymer demand in the world by volume was from PP (**Figure 2**) [5].

2. Synthesis and functionalization

Well-defined polymers with narrow polydispersity and controlled molecular weight are essential to delineate the structure–property relationship of polymeric materials [6]. Using N,N-diethyl hafnium derivative as active transition metal propagation center and $ZnEt_2$ as metal alkyl chain transfer agent, Sita first demonstrated the living coordinative chain transfer polymerization of propene to produce amorphous atactic polypropylene (a-PP) with narrow polydispersity and various molecular weights from 12.6 kDa to 111 kDa [7]. Compared with a-PP, isotactic polypropylene (iPP) is more practical for applications in packaging and automotive parts. Coates designed a pyridylamidohafnium catalyst that produced PP with high iso-selectivity (91%) and living polymerization behavior (**Figure 3**) [8]. The study also confirmed a ligand-monomer interaction as the mechanism of stereo-control. The progress of using coordinative chain transfer polymerization has been thoroughly reviewed elsewhere [9, 10].

Block copolymers have contributed significantly to thermoplastic elastomers, soft lithography, and drug delivery [11]. Block copolymers containing polypropylene can serve as a compatibilizer to improve the interface interaction between polyolefin and other polar materials. Chen demonstrated an early example of polypropylene-block-poly(methyl methacrylate) (PP-b-PMMA) diblock copolymer using Group IV metal catalyst [12]. By taking advantage of the solubility, the



2019 PureCycle Technologies successfully purified waste carpet into clear, odorless Ultra-Pure Recycled Polypropylene (UPRP) resin**

1997 Montell (now LyondellBasell) commercializes PP using 5th generation ZN catalysts

1995 ExxonMobil and others commercialized PP using single-site catalysts

1986 Union Carbide (now Dow) commercialized Unipol® gas phase process for PP

1980 Sumitomo Chemical commercialized bulk polymerization process for PP*

1976 Kaminsky, Sinn and coworkers discovered high activity metallocene using MAO cocatalyst

1975 3rd Generation catalysts commercialized by Montecatini, Shell and other companies

1957 Commercial production of PP in Italy, Germany and USA

1954 Nata synthesized stereoregular PP using Ziegler-Nata catalyst

1951 Hogan and Banks discovered "solid" PP using chromium catalyst

Figure 1.
Key milestones of the commercialization of polypropylene. Adapted from Ref. [1-4].

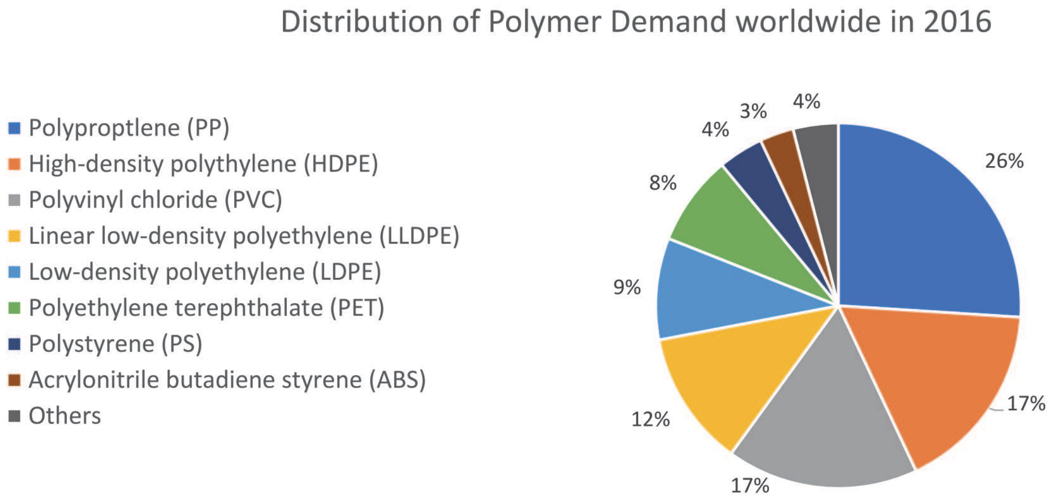


Figure 2.
Distribution of polymer demand worldwide in 2016 by volume. Adapted from Ref. [5].

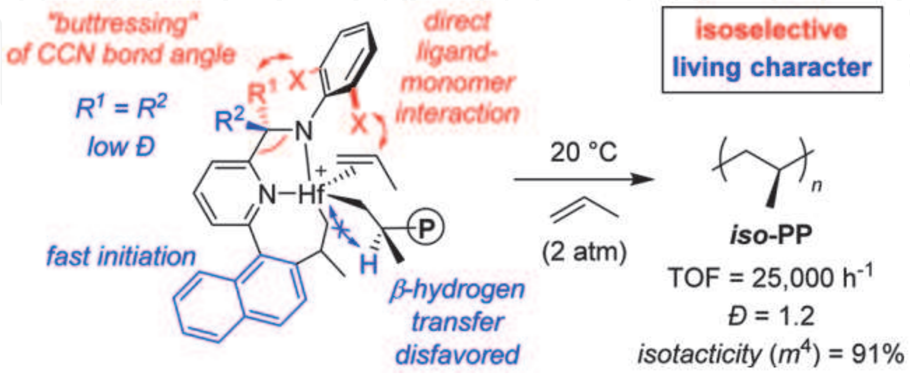


Figure 3.
Living and iso-selective propylene polymerization (reprinted with permission from Ref. [8]. Copyright 2017 American Chemical Society).

resulting polymer could be purified into narrow distributed copolymers with hexane-heptane fractionation. Dong et al. used a brominated isotactic PP with styrene termination as a macroinitiator to copolymerize styrene or methyl

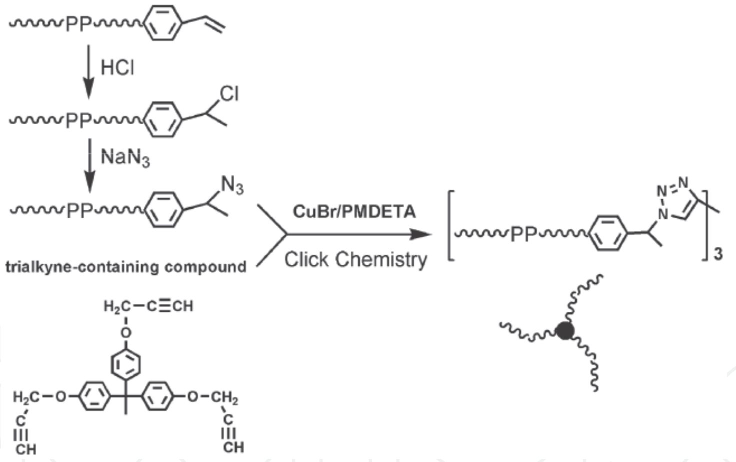


Figure 4.
Synthesis of three-arm PP star polymer by click chemistry (reprinted with permission from Ref. [14]. Copyright 2010 American Chemical Society).

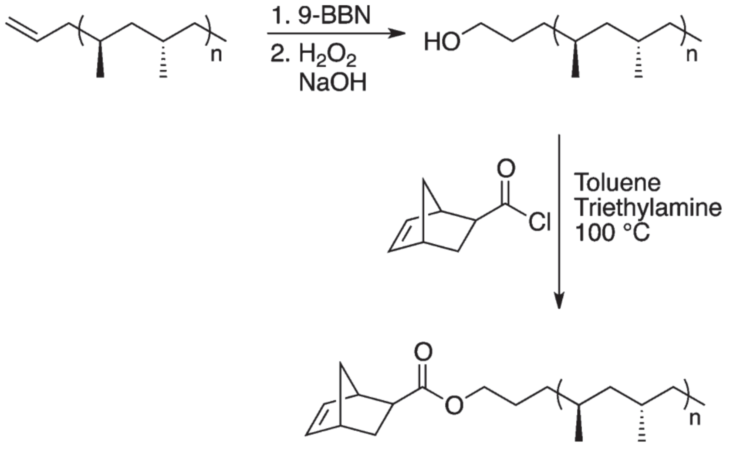


Figure 5.
Synthesis of PP comb polymers (reprinted with permission from Ref. [20]. Copyright 2012 American Chemical Society).

methacrylate and studied the blending behavior between the resulting copolymers with PS/PP or PMMA/PP blend [13]. The same group prepared azide end-functionalized PP and prepared PP three-arm star polymer (**Figure 4**) [14] and PP-b-polycaprolactone (PP-b-PCL) block copolymers [15]. By terminating the coordination polymerization of iPP with (p-vinylphenyl)chlorosilane, iPP star polymers with 3–8 different numbers of arms were prepared in an H_2O/toluene emulsion system [16].

Using stereoselective insertion polymerization catalyst, Coates synthesized a group of block copolymers containing iPP as the rigid block and regioirregular polypropylene (rPP) as the elastic block. The mechanical characterization of the iPP-rPP-iPP-rPP-iPP pentablock copolymer indicated a strain at break of 2400% and a maximum true tensile stress of 250 MPa [17]. In collaboration with Bates and LaPointe, the group synthesized a polyethylene-b-iPP-b-polyethylene-b-iPP tetrablock copolymer and evaluated the blending behavior of the tetrablock copolymer with PE/iPP. By “welding” polyethylene (PE) and iPP, together with the tetrablock copolymer, previously impossible due to the immiscibility, the blend was transformed from a brittle glass into a tough plastic, paving a possibility to recycle the world’s two most-produced polymer materials [18].

Long-chain branching in polymers has shown interesting rheological behaviors [19]. Using norbornene-terminated syndiotactic PP as a macromonomer, Coates synthesized a group of well-defined s-PP bottlebrush polymers with a molecular weight from 46 kDa to 172 kDa using Grubbs' metathesis catalyst (**Figure 5**) [20]. A decrease in both melting and crystallization temperature was observed and attributed to the constraints on the rigid backbone. Further research by Bates and Hillmyer revealed a scaling transition that depends on the length of the backbone [21]. Hazer evaluated the surface property and mechanical property of a group of graft copolymer containing polypropylene as the backbone and polyethylene glycol (PEG) as the side chain [22]. With 15% of PEG, the graft copolymer demonstrated ultimate stress of 22 MPa and elongation at break of 670%. Bielawski developed a direct C—H azidation method to introduce azide functionalities into commercially available PP [23] and prepared PP-g-PEG using click chemistry. Tasdelen used a similar approach and synthesized PP-g-PCL copolymers [24].

"Reactive" polyolefin approach, adding functional monomer units into the polyolefin chain, has emerged as a powerful tool to chemically functionalize polyolefins [25]. Pan copolymerized p-(3-butenyl)styrene and propylene with (pyridylamido)Hf/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ catalytic system, which selectively copolymerize α-olefin over styrene [26]. The pendant styrenic vinyl groups in the resulting polymer were quantitatively converted into carboxylic acid groups with thiol-ene addition. The same group further extended this methodology to prepare amino-containing iPP, which exhibited high thermal stability and melting temperature [27]. Chung synthesized a group of hydroxyl-functionalized PP using silane-protected 10-undecen-1-ol as a comonomer and converted the hydroxyl pendant group into butylated hydroxytoluene (BHT) derivatives (**Figure 6**) [28]. The resulting BHT-functionalized PP demonstrated improved thermal stability and higher dielectric constant. With two methylene group spacers between BHT and ester linkage, the materials displayed superior thermal stability at 190°C compared with general and capacitor grade PP [29].

Polypropylene is one of the most important plastics in our daily life. However, the materials itself also caused a significant amount of plastic pollution. As much exciting progress has been achieved recently to introduce functionalities and improve both mechanical and thermal stabilities, the research community should also emphasize on developing approaches to recycle PP and PE from the processed product.

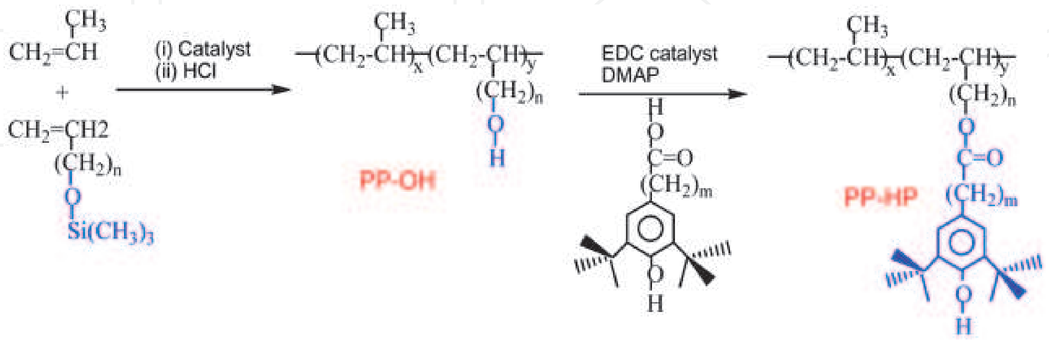


Figure 6.
Synthesis of BHT-functionalized PP (reprinted with permission from Ref. [28]. Copyright 2015 American Chemical Society).

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