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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

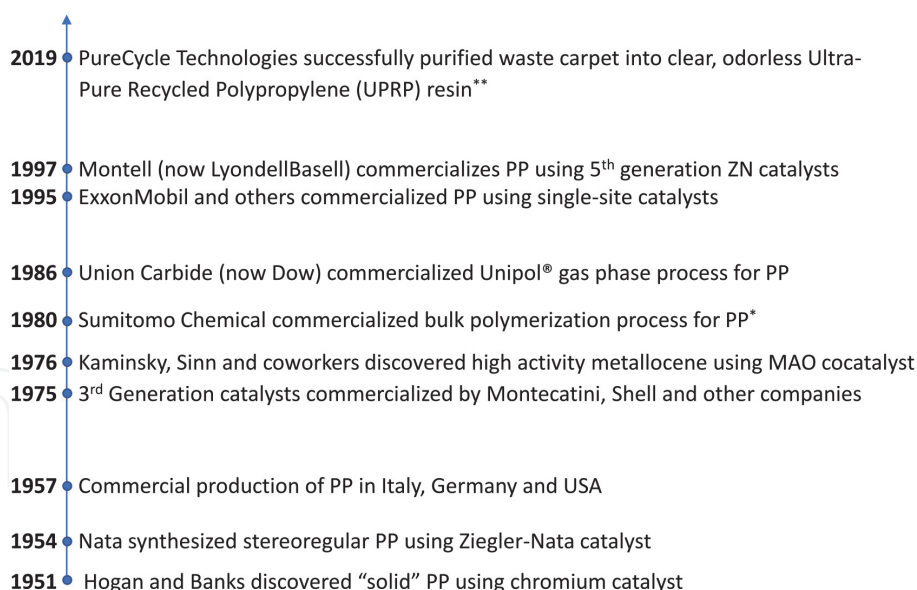


Figure 1.
Key milestones of the commercialization of polypropylene. Adapted from Ref. [1-4].

Distribution of Polymer Demand worldwide in 2016

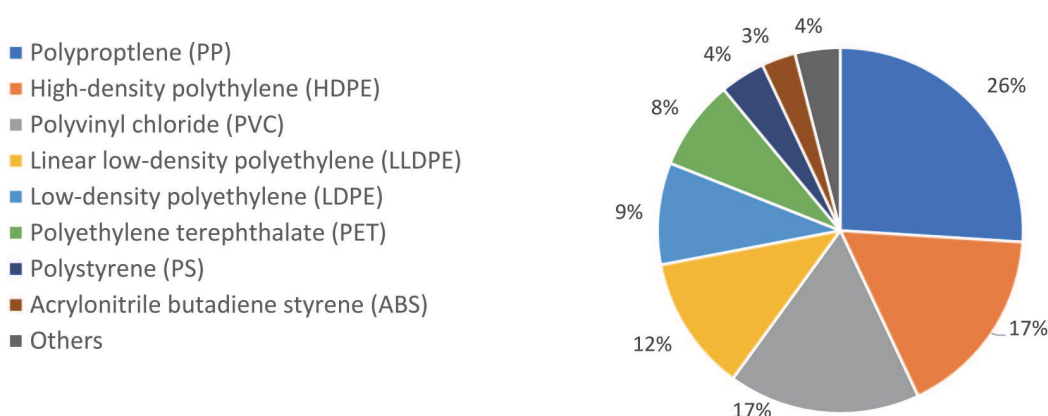


Figure 2.
Distribution of polymer demand worldwide in 2016 by volume. Adapted from Ref. [5].

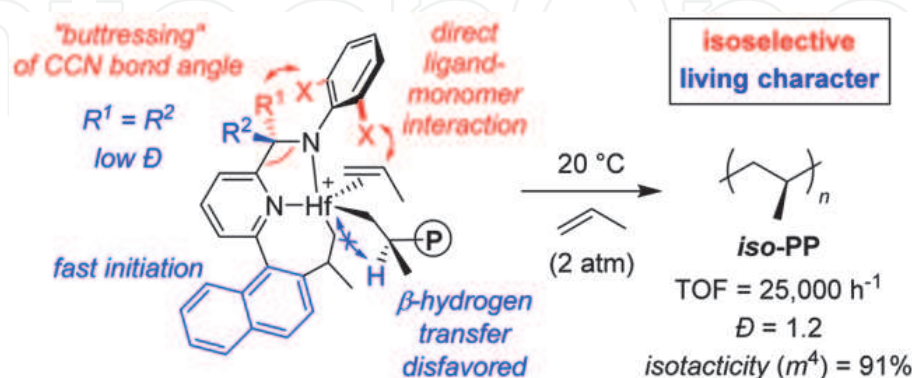


Figure 3.
Living and iso-selective propylene polymerization (reprinted with permission from Ref. [8]. Copyright 2017 American Chemical Society).

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

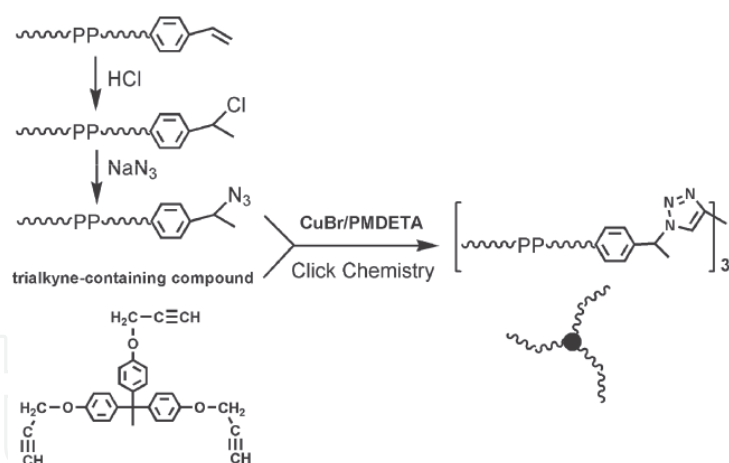


Figure 4.
 Synthesis of three-arm PP star polymer by click chemistry (reprinted with permission from Ref. [14]. Copyright 2010 American Chemical Society).

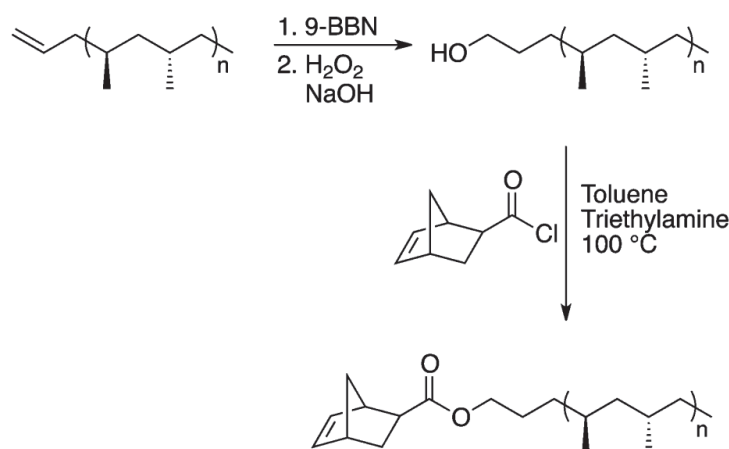


Figure 5.
 Synthesis of PP comb polymers (reprinted with permission from Ref. [20]. Copyright 2012 American Chemical Society).

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 H₂O/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/[Ph₃C][B(C₆F₅)₄]/AlⁱBu₃ 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.

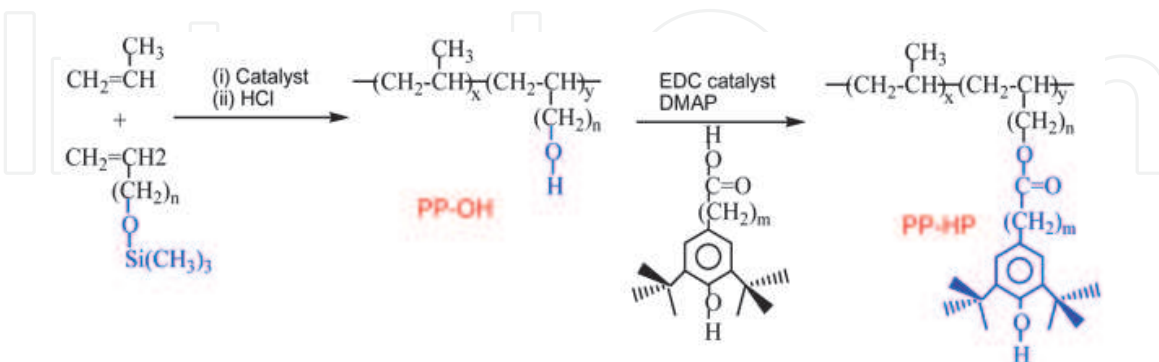


Figure 6.

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

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References

- [1] Stinson S. Discoverers of polypropylene share prize. *Chemical & Engineering News*. 1987;**65**(10):30. DOI: 10.1021/cen-v065n010.p030
- [2] Dennis B. Malpass, Elliot I. Band. Introduction to polymers of propylene. In: Dennis B. Malpass, Elliot I. Band, editors. *Introduction to Industrial Polypropylene: Properties, Catalysts Processes*. 1st ed. John Wiley & Sons; 2012. p. 1-18. DOI: 10.1002/9781118463215
- [3] Sato H, Ogawa H. Review on Development of Polypropylene Manufacturing Process. Vol. 12. Sumitomo Chemical Co., Ltda, Process and Production Technology Center. Tokyo, Japan: Fecha de consulta; 2009
- [4] PureCycle Technologies. PureCycle Technologies Celebrates Successful Run of Groundbreaking Plastics Recycling Technology [Internet]. September 2019. [Updated: September 2019]. Available from: <https://purecycletech.com/2019/09/successful-run-of-feedstock-evaluation-unit/> [Accessed: March 2020]
- [5] Statista. Plastic industry worldwide [Internet]. January 2020. [Updated: January 2020]. Available from: <https://www.statista.com/study/51465/global-plastics-industry/> [Accessed: March 2020]
- [6] Lutz J-F. 100th anniversary of macromolecular science viewpoint: Toward artificial life-supporting macromolecules. *ACS Macro Letters*. 2020;**9**:185-189. DOI: 10.1021/acsmacrolett.9b00938
- [7] Zhang W, Sita LR. Highly efficient, living coordinative chain-transfer polymerization of propene with ZnEt_2 : Practical production of ultrahigh to very low molecular weight amorphous atactic polypropylenes of extremely narrow polydispersity. *Journal of the American Chemical Society*. 2008;**130**(2):442-443. DOI: 10.1021/ja078120v
- [8] Domski GJ, Eagan JM, De Rosa C, Di Girolamo R, LaPointe AM, Lobkovsky EB, et al. Combined experimental and theoretical approach for living and Isoselective propylene polymerization. *ACS Catalysis*. 2017;**7**(10):6930-6937. DOI: 10.1021/acscatal.7b02107
- [9] Valente A, Mortreux A, Visseaux M, Zinck P. Coordinative chain transfer polymerization. *Chemical Reviews*. 2013;**113**(5):3836-3857. DOI: 10.1021/cr300289z
- [10] Stürzel M, Mihañ S, Mülhaupt R. From multisite polymerization catalysis to sustainable materials and all-polyolefin composites. *Chemical Reviews*. 2016;**116**(3):1398-1433. DOI: 10.1021/acs.chemrev.5b00310
- [11] Feng H, Lu X, Wang W, Kang NG, Mays JW. Block copolymers: Synthesis, self-assembly, and applications. *Polymers*. 2017;**9**(10):494. DOI: 10.3390/polym9100494
- [12] Jin J, Chen EY-X. Stereoblock copolymerization of propylene and methyl methacrylate with single-site metallocene catalysts. *Macromolecular Chemistry and Physics*. 2002;**203**(16): 2329-2333. DOI: 10.1002/macp.200290010
- [13] Zhang L-Y, Fan G-Q, Guo C-Y, Dong J-Y, Hu Y-L, Huang M-B. Synthesis of polypropylene block copolymers from brominated styrene-terminated isotactic polypropylene. *European Polymer Journal*. 2006;**42**(5):1043-1050. DOI: 10.1016/j.eurpolymj.2005.11.021
- [14] Huang H, Niu H, Dong J-Y. Synthesis of star isotactic polypropylene using click chemistry. *Macromolecules*. 2010;**43**(20): 8331-8335. DOI: 10.1021/ma1019335
- [15] Huang H, Niu H, Dong J-Y. Synthesis of azide end-functionalized

isotactic polypropylene building block and renewed modular synthesis of diblock copolymers of isotactic polypropylene and poly (ϵ -caprolactone). *Journal of Polymer Science Part A: Polymer Chemistry*. 2011;**49**(10):2222-2232. DOI: 10.1002/pola.24653

[16] Liu X, Niu H, Yang L, Dong J-Y. New effort to synthesize star isotactic polypropylene. *Polymer Chemistry*. 2018;**9**(24):3347-3354. DOI: 10.1039/C8PY00318A

[17] Hotta A, Cochran E, Ruokolainen J, Khanna V, Fredrickson GH, Kramer EJ, et al. Semicrystalline thermoplastic elastomeric polyolefins: Advances through catalyst development and macromolecular design. *Proceedings of the National Academy of Sciences*. 2006;**103**(42):15327-15332. DOI: 10.1073/pnas.0602894103

[18] Eagan JM, Xu J, Girolamo RD, Thurber CM, Macosko CW, AMLaPointe FSB, et al. Combining polyethylene and polypropylene: Enhanced performance with PE/iPP multiblock polymers. *Science*. 2017; **355**(6327):814-816. DOI: 10.1126/science.aah5744

[19] Lagendijk RP, Hogt AH, Buijtenhuijs A, Gotsis AD. Peroxydicarbonate modification of polypropylene and extensional flow properties. *Polymer*. 2001;**42**(25): 10035-10043. DOI: 10.1016/S0032-3861(01)00553-5

[20] Anderson-Wile AM, Coates GW, Auriemma F, De Rosa C, Silvestre A. Synthesis and ring-opening metathesis polymerization of norbornene-terminated syndiotactic polypropylene. *Macromolecules*. 2012;**45**(19): 7863-7877. DOI: 10.1021/ma301073s

[21] Dalsin SJ, Hillmyer MA, Bates FS. Molecular weight dependence of zero-shear viscosity in atactic polypropylene

bottlebrush polymers. *ACS Macro Letters*. 2014;**3**(5):423-427. DOI: 10.1021/mz500082h

[22] Balci M, Allı A, Hazer B, Güven O, Cavicchi K, Cakmak M. Synthesis and characterization of novel comb-type amphiphilic graft copolymers containing polypropylene and polyethylene glycol. *Polymer Bulletin*. 2010;**64**(7):691-705. DOI: 10.1007/s00289-009-0211-3

[23] Liu D, Bielawski CW. Direct azidation of isotactic polypropylene and synthesis of 'grafted to' derivatives thereof using azide-alkyne cycloaddition chemistry. *Polymer International*. 2017;**66**(1):70-76. DOI: 10.1002/pi.5180

[24] Acik G, Sey E, Tasdelen MA. Polypropylene-based graft copolymers via CuAAC click chemistry. *eXPRESS Polymer Letters*. 2018;**12**(5):418-428. DOI: 10.3144/expresspolymlett.2018.35

[25] Chung TCM. Functional polyolefins for energy applications. *Macromolecules*. 2013;**46**(17): 6671-6698. DOI: 10.1021/ma401244t

[26] Wang X-Y, Wang Y-X, Li Y-S, Pan L. Convenient syntheses and versatile functionalizations of isotactic polypropylene containing plentiful pendant styrene groups with high efficiency. *Macromolecules*. 2015;**48**(7): 1991-1998. DOI: 10.1021/acs.macromol.5b00128

[27] Shang R, Gao H, Luo F, Li Y, Wang B, Ma Z, et al. Functional isotactic polypropylenes via efficient direct copolymerizations of propylene with various amino-functionalized α -olefins. *Macromolecules*. 2019;**52**(23): 9280-9290. DOI: 10.1021/acs.macromol.9b00757

[28] Zhang G, Li H, Antensteiner M, Mike Chung TC. Synthesis of functional polypropylene containing hindered

phenol stabilizers and applications in metallized polymer film capacitors. *Macromolecules*. 2015;**48**(9):2925-2934. DOI: 10.1021/acs.macromol.5b00439

[29] Zhang G, Changwoo N, Mike Chung TC, Petersson L, Hillborg H. Polypropylene copolymer containing cross-linkable antioxidant moieties with long-term stability under elevated temperature conditions. *Macromolecules*. 2017;**50**(18):7041-7051. DOI: 10.1021/acs.macromol.7b01235