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Extending Alkenes' Value Chain to Functionalized Polyolefins

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Abstract

Naphtha is one of the crude oil distillation products, bringing almost the lowest value-addition to crude oil, compared to other refinery products such as liquid petroleum gas, gasoline, and diesel. However, Naphtha can be converted to one of the highest value products at the end of the value chain, i.e., polyolefins. Although the production of conventional commodity polyolefins from crude oil, is considered as one of the final products in alkenes' value chain, there are specialty polyolefins with higher values. Specialty polyolefins are small volume, high-performance thermoplastics with high-profit margins compared to traditional commodity polyolefins. Recently, some special purpose functionalized polyolefins have been developed as efficient substituents for high-performance engineering thermoplastics. Polyolefins are exploited as cost-effective platforms to produce these functionalized thermoplastics. They are promising candidates for replacing high-performance polymers with high-cost raw materials and elaborate production processes. So, functional polyolefins have introduced a new paradigm in the production of high-performance thermoplastics, extending the alkenes' value chain and increasing profitability. High-performance specialty polyolefins may find exceptional markets in niche applications. In this chapter, the commercial specialty and functional polyolefins' current situation and prospects are reviewed.

Keywords: Alkenes' value chain, specialty polyolefins, niche markets, functional polyolefins, single-site catalysts, insertion polymerization

1. Introduction

The value chain notion refers to all value-creating activities, potential developments, and opportunities in industrial production, from the raw materials to the goods delivered to the final consumers. It is an appropriate base for the creation of strategic niches. The concept of niches corresponds to innovative studies and is used in different ways. Commonly, it is related to the emerging new technology-based markets. New strategic niches are the main origins of pioneering innovations. The path-breaking works deviate from the dominant routes because of their production technology and markets. Although strategic niches may lack well-defined market in their emerging phase, some actors supply the essential resources with high expectations about the technology economy and sustainability.

The sustainability transition and radical shifts toward the value-added products in the petrochemical industry are hindered by difficulties in the production

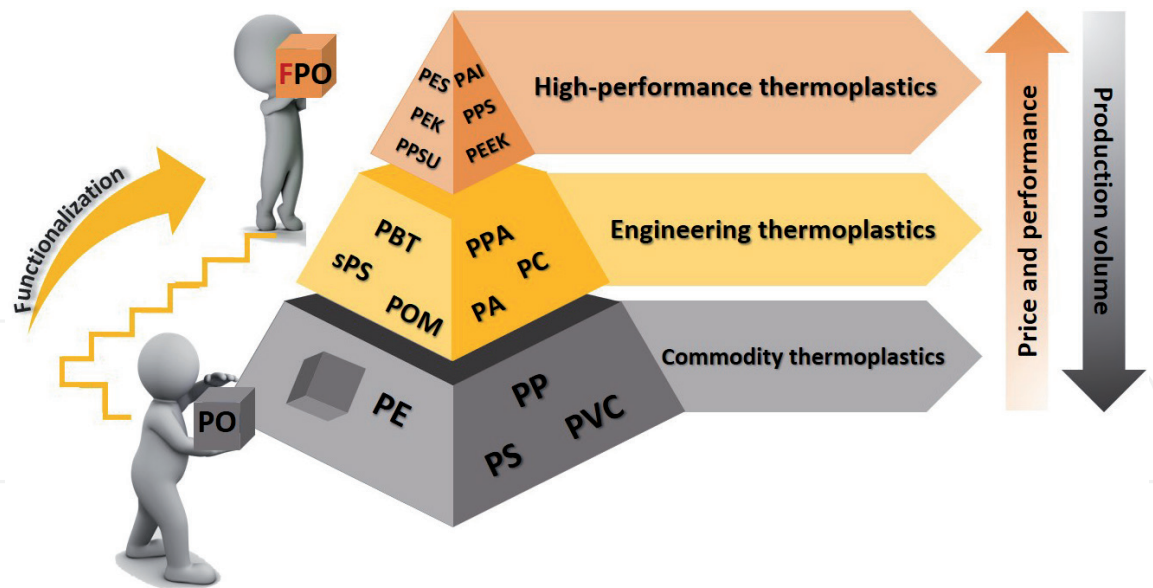


Figure 1. Olefin-based functional co- or terpolymers as cost-effective high-quality substituents for high-performance thermoplastics.

trajectory due to the lack of well-established value chains. Besides the separated links, the lack of cross-chain interactions and connections between the suppliers and end-users hamper the petrochemical industry performance, too.

This chapter aims to evaluate how specialty polyolefins may accelerate innovative and sustainable research in industrial and/or academic areas. **Figure 1** demonstrates the thermoplastics triangle and the state of functional polyolefins, to enlighten the techno-scientific importance of emerging new products and their added value.

2. Alkenes’ value chain

The alkenes’ value chain starts with Naphtha or ethane (**Figure 2**). Alkenes are mainly converted to polyolefins (e.g., up to 60 wt% of ethylene converted to

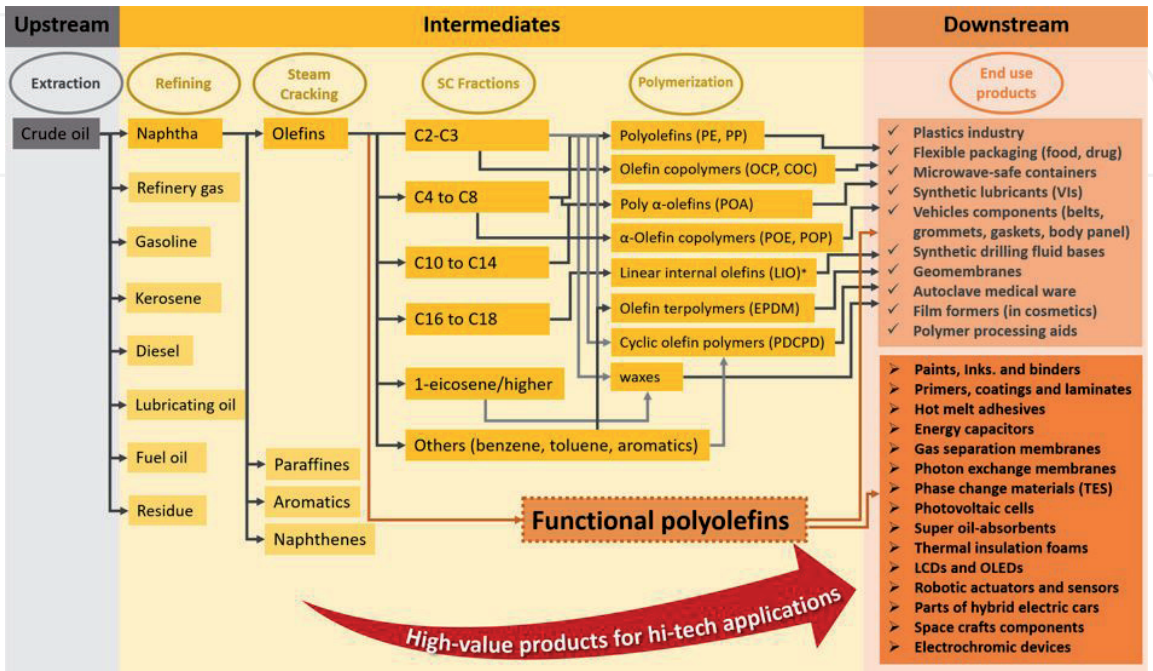


Figure 2. Alkenes’ value chain. * Isomerization product.

polyethylene), valued to have the largest market with more than 50 wt% of the synthetic polymers and 300 current commercial grades [1, 2]. In the downstream, polyolefin grades are converted to end-products.

The present study is focused on specialty polyolefins production, applications, challenges and future trends. Specifically, we want to answer the following questions. a) what is the potential value of specialty polyolefins? b) what are the essential requirements in taking full advantage of these value-added polyolefins? c) what are the trends and elements of the future of functional polyolefins?

3. Polyolefins' "Golden age"

Nowadays, polyethylene and polypropylene, as the most popular, widespread, and predominantly produced commodity polymers, account for approximately 32 and 27% of the global polymer market, with an annual growth rate of 4.0% and 5.3% within the forecast period of 2019 to 2027, respectively [3]. With a global market value of \$300 billion and volume of 180 million tons they play an important role in our daily life [4].

The "Golden age" of polyolefins started with the seminal discovery of the Nobel Prize winners, Prof. Karl Ziegler and Prof. Giulio Natta, which was followed by finding the magical role of methyl aluminoxane in the activation of single-site transition metal catalysts, by Prof. Walter Kaminsky and Prof. Hansjörg Sinn. Then, the late transition metal catalysts bearing α -diamine ligands were introduced by Prof. Maurice Brookhart. These catalysts benefited by their exceptionally high activity, besides high tolerance toward heteroatom-containing moieties, which genuinely elevates polyolefins value to a higher level than the corresponding traditional grades [5–7].

Standing on the shoulders of the giants, the past 70 years of polyolefins technology progress has been summed up in the discovery of new catalysts accompanied with the development of new industrial polymerization processes [8, 9]. As low-cost thermoplastics, polyolefins gain the attention of researchers as an abundant platform for the production of specialty and functional polyolefins [10, 11]. The worldwide interest in specialty polyolefins and research outputs by regions over the last two decades is presented in **Figure 3**.

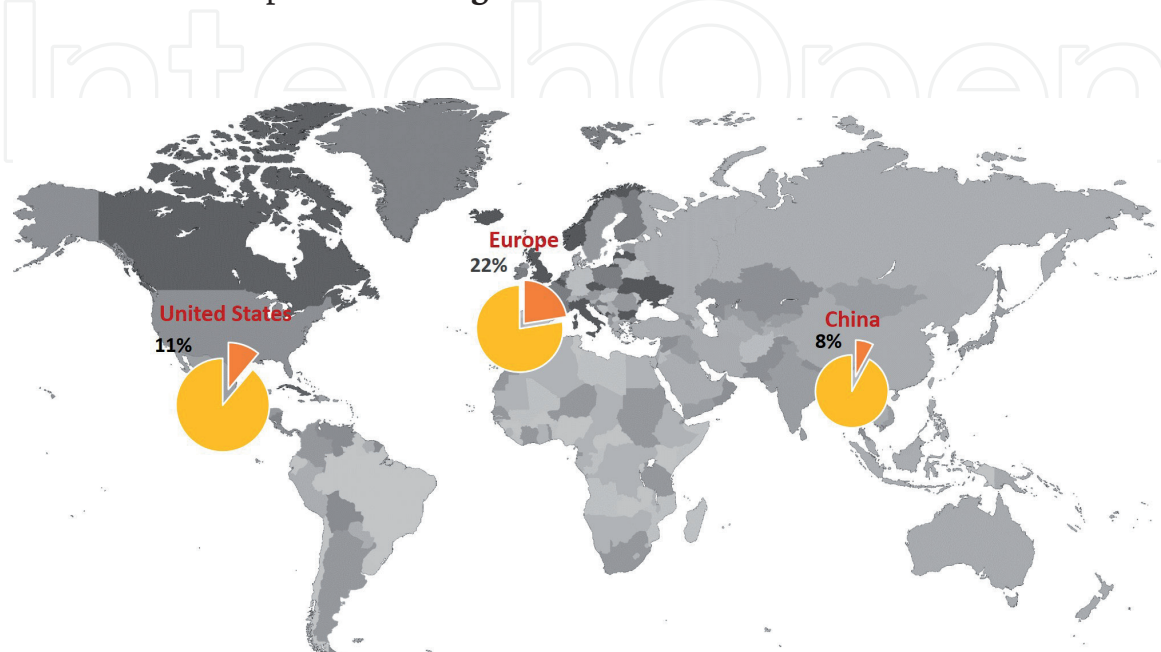


Figure 3.
Worldwide scientific interest in functional and specialty polyolefins in the last two decades.

4. Applications and niche markets of specialty polyolefins

Until 30 years ago, the physical properties of polyethylene such as density and melt index values as well as chemical characteristics i.e., inherent hydrophobicity were limited. However, the innovative single-site catalysts have removed the barriers and polyethylene products with lower densities became available. Generally, such polyethylene grades are ethylene- α -olefin copolymers where α -olefin content exceeds 40 wt% in some cases and results in elastomeric properties. In addition, ethylene-cyclic olefin (e.g., norbornene or cyclopentadiene) copolymers, also known as specialty polyolefins, extend the polyolefin properties boundaries and the alkenes' value chain.

On the other side, according to their non-polar nature, commercial polyolefins suffer from a lack of adhesion, printability, wettability, reactivity, compatibility, and miscibility. Hence, applying such an intrinsically hydrophobic polymer as an adhesive, coating, paint, primer, or binder is restricted. Also, the poor interaction of polyolefins with other materials like paints, pigments, glass fibers, clay, carbon black, metals, and the vast majority of polymers limited their applications in blends and composites [5].

However, incorporating functional groups on the polyolefin chain, even at the chain-ends, branch-ends or backbone, leads to the enhancement of polyolefins' adhesion and binding properties, which opens up exciting industrial application fields. So far, functional polyolefins' applications comprised of binders in book-binding, glue in adhesives, printing inks, tie-layer in multilayer sheets or films, and compatibilizer in blends of polar and non-polar polymers. Interestingly, they may open up new possibilities for application in film capacitors with superior energy density, proton exchange membranes for fuel cells and super-absorbents suitable for the oil spills (without any water) absorption [12].

Herein, commercially available specialty polyolefins, including functional olefin copolymers as valuable extenders of the alkenes' value chain, are comprehensively reviewed. Some of the structures of value-added polyolefins presented in this chapter are shown in **Figure 4**.

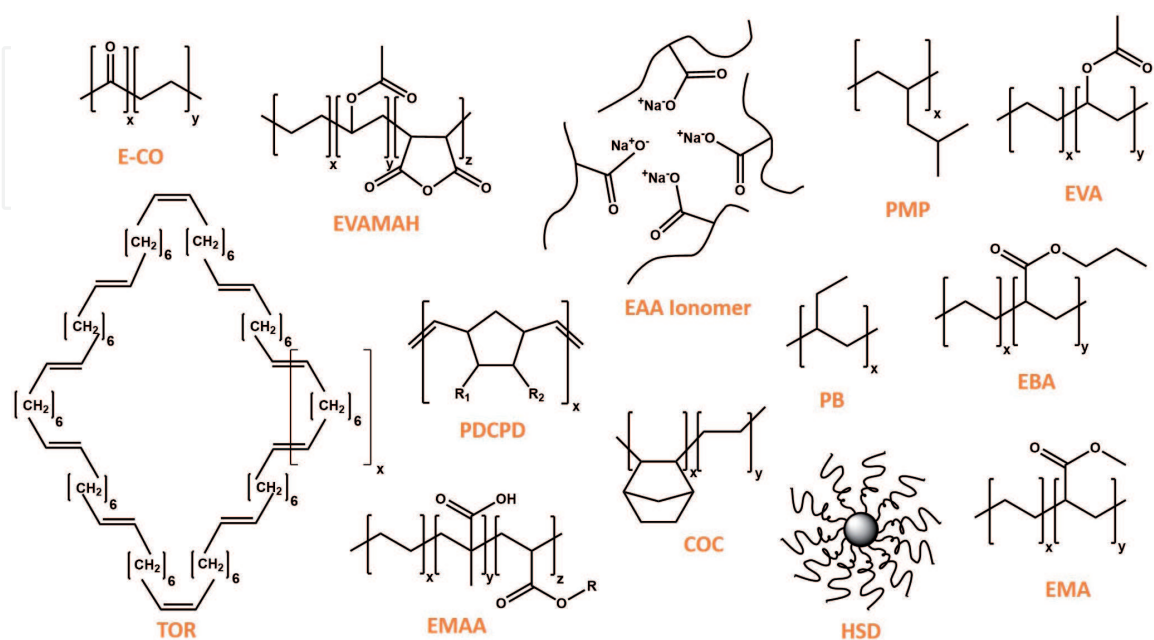


Figure 4. The chemical structure of some of the specialty polyolefins with niche applications which will be discussed in this chapter.

4.1 α -Olefin (co)polymers

Poly(1-butene) (PB) or polybutylene is a specialty polyolefin with niche applications. This stereospecific (isotactic), linear, high molecular weight, low density, and crystalline thermoplastic has extraordinary creep, abrasion, and environmental stress cracking resistance besides superior chemical inertness. According to its unique properties and performance, some of the niche applications of this poly α -olefin include pressurized hot- and cold-water pipes, hot-water blow-molded tanks, plumbing, and heating systems [2]. Moreover, since PB has good compatibility with most of the tackifiers, it is used in hot melt adhesive formulations, especially to increase the sticky "open time" [13]. Also, PB/PE blends are utilized in easy open flexible packaging technology.

Recently, some PB composites with high dielectric constant and break downfield strength besides low dielectric loss are reported, which are susceptible to application in capacitors [14].

Hydrogenated poly(1-butene) (HPB) is a safe polyene and can be used as an ingredient in cosmetics [15]. It is used at lower molecular weights (400–1000 Daltons) in lip gloss formulations since such polyene is very shiny and possessing good adhesion to lip surfaces. Other applications of HPB in cosmetics include eye makeup, eyeliner, blushes, and foundation [16].

Hydrogenated poly(1-decene) (HPD) is commonly used as a film former in cosmetic formulations. HPDs are available in a wide range of viscosities and are used in skincare, eye shadow, makeup, and lip products due to their non-greasy skin feel [16]. The catalytic oligomerization of 1-decene to tri-, tetra-, and penta-decene chains followed by hydrogenation, results in the production of this polyene. It is available under the tradename of PAO 4–8 by Chevron Philips. Since this polyene is of low acute toxicity and does not raise concern for genotoxicity, it can be used as an ingredient in foods, such as glazing or polishing agent for dried fruits [15, 17]. Other applications of HPD are release coating in bread and loaf pans, lubricant in automatic dough dividers, anti-dusting and anti-foaming agents, and plasticizer in food contact films [18].

Although 4-methyl-1-pentene is one of the comonomers used in linear low-density polyethylene production, **poly(4-methyl-1-pentene) (PMP)** is a commercially available specialty engineering polyolefin under the trade name of TPX™. PMP has extremely low density (0.835 g/ml) and surface energy, excellent heat resistance, and chemical inertness besides high transparency, optical and acoustic properties. The industrial applications of PMP include mandrels and sheaths in high-pressure rubber hose fabrication, release films and papers in synthetic leather production, and LED light mold cups. The extremely low density of PMP makes it as a good candidate for automotive parts due to its lower weight and environmental load. Moreover, it is used in several food-related articles, e.g., baking boxes, food packs and wraps, and microwave-safe dishes [2].

Also, it is suitable for applications where transparency and heat resistance are required, e.g., autoclave medical and laboratory ware, microwave and oven components, and heat resistant wire and cables. Furthermore, since PMP is incompatible with some of the thermoplastics (e.g., poly (ethylene terephthalate)), it is used to create porous PET structures [19].

On the other side, PMP is commercially available as hollow fibers (HFs) used in gas separation membranes, where the gas permeability derived from its molecular microstructure. As it was reported recently, the transport and separation performance of these HFs improved by PMP's crystallinity increment [20].

Ring-opening metathesis polymerization (ROMP) of cyclooctene gives **polyoc-tenamers** which are marketed under the name of Vestenamer. They are the world's

most versatile rubber additive used for years. As a semicrystalline, double bond containing polyolefin additive, trans-polyoctenamers (TORs) act as plasticizers in rubber compounding and processing. The cis/trans ratio of polyoctenamers, which is controlled during the polymerization, determines the degree of crystallinity. Generally, the higher the trans content, the higher the crystallinity and melting point. Also, the extremely high crystallization rate of polyoctenamers is advantageous in the soft compounds cold flow reduction, improving green strength, or reducing shrinkage during calendaring.

Since polyoctenamers take part in the vulcanization process, one may consider them as reactive plasticizers. Also, the high macrocycle content of polyoctenamers reduces their molecular weight significantly. In addition to the low molecular weight, the broad molecular weight distribution of polyoctenamers is responsible for their unusual low viscosity at elevated temperatures. Polyoctenamers enable the compounding of incompatible polymers (e.g., NBR and EPDM), reduce viscosity, heat build-up, mix time and energy intake, improve dimensional stability, quality and filler acceptance, and increase throughput.

Furthermore, polyoctenamers allow efficient processing of waste rubbers into tough materials to be used again, i.e., effective in rubber sustainability [21].

Vistamaxx is the trade name of **propylene-ethylene copolymer (PEC)** produced using metallocene catalysts by ExxonMobil Chemicals, comprised of isotactic propylene blocks with random ethylene distribution where the propylene content is over 70 mol%. This copolymer's chemical structure and properties are intermediate between amorphous ethylene-propylene rubber and semi-crystalline isotactic polypropylene [22]. Considering PEC's good processability and compatibility with a wide range of polyolefins, and very low viscosity, it is used as an ingredient in hot melt adhesives (accounts for up to 70–90% of the mixture providing high-performance HMAs with tunable “open-time”) and as a processing aid or viscosity improver in extrusion or injection molding processes to improve the flow characteristics.

Consequently, PEC enhances polyolefin blend properties to deliver improved impact strength, higher flexibility, enhanced esthetics, and lower stress-whitening. Also, it is employed as a sealing layer in co-extruded articles due to its extremely low seal initiation temperature combined with high seal strength. This copolymer is a suitable substituent for wax in masterbatch formulations, optimizing costs by lowering the cycle time. Moreover, the color strength increased in the presence of such copolymer by almost 20% because of its high compatibility with polyethylene and polypropylene and well pigment wetting and dispersion at lower processing temperatures [23–25].

Moreover, using Vistamaxx as a minor component (up to 20 wt%) in spunmelt nonwovens designed for applications such as leg barrier cuffs, diapers and medical gowns results in improved softness [26].

Olefin copolymer (OCP) viscosity improvers (VIs) are mainly ethylene-propylene copolymers with ethylene to propylene ratio of 45/55–55/45 synthesized using Ziegler-Natta and metallocene catalysts. Short ethylene sequences in OCPs, are crystallized into fringed micelles while higher-ordered morphologies, i.e., lamellae or spherulites, are absent in such copolymers. Also, the fraction of EE sequences (dyads) and the average length of contiguous ethylene units are raised by increasing the ethylene to propylene ratio. Due to the limited solubility of such OCPs in most mineral oils and consequently the inappropriate function of OCP as VI, the degree of crystallinity should not exceed 25% in OCP VIs [27]. Therefore, the physical properties of OCPs fall in between the characteristics of semicrystalline polyethylene and amorphous ethylene-propylene rubber. This oil-soluble copolymer cold flows at room temperature and improves the low-temperature rheology, thickening efficiency, and bulk handling characteristics of engine oils.

Moreover, some essential functions such as dispersing contaminants, antioxidative stabilization, and antiwearing are combined with the rheology control features on the same molecule by OCPs functionalization. Some hybrids have been commercialized, including dispersant OCPs, dispersant antioxidant OCPs, and ashless antiwear dispersant OCPs. These hybrid lubricants are produced through different methods. The most attractive approaches are free radical grafting of nitrogen-containing monomers such as phenothiazine to provide antioxidant functionality and two-step grafting method. In the second approach, maleic anhydride (or such diacyls) is grafted onto the OCP molecule. Then the amine or alcohol reacts with the anhydride to create imide, amide or ester bonds. Also, many functional OCPs have been described in the patents [28–30].

The future perspective of OCPs includes optimizing viscosity ranges, improving the shear stability of the formulations, and designing novel tailor-made functional OCPs (FOCPs) as low cost, highly efficient, and customer choice multifunctional VIs [27].

Ethylene-propylene-diene terpolymers (EPDMs) industrial production returns to the 1960s by ExxonMobil Chemical Company, which was designated as Vistalon™. The development of this terpolymer was a natural evolution of Ziegler-Natta technology after the production of other polyolefins. The saturated backbone of EPDM, compared to other rubbers, and consequently its excellent ozone, environmental, and weather resistance makes it the material of choice in the production of various outdoor articles. Typical applications of EPDM include the automotive industry (weather seals, radiator hose, gaskets, grommets, O-rings, belts), construction industry (single-ply roofing material, geomembranes), electrical devices (wire and cable covers), polymer modification (polymer blends used in automotive bumpers), oil modifiers and so on [31, 32].

Based on developments in Daw Chemicals catalyst technology, novel grades of EPDM, i.e., ultrahigh molecular weight EPDM, known as (UHMW)NORDEL™ were developed. NORDEL is highly efficient in producing thermoplastic vulcanizates (TPVs), light color home appliance gaskets, and black color low hardness molded articles [33, 34].

Recently, the potential future applications of novel paraffin-filled EPDM foams as phase change materials (PCMs) in thermal energy storage (TES) systems have been investigated [35, 36].

4.2 Cyclic olefin (co)polymers

As a successful example, **ethylene-norbornene copolymers**, well-known as COCs, are synthesized via the copolymerization of ethylene with norbornene (or cyclopentene) using metallocene complexes. COCs are glossy, transparent, rigid and amorphous thermoplastics commercially available by TOPAS Advanced Polymers, Inc. The low shrinkage and high modulus (due to the high norbornene content of about 30–60 mol%) of this copolymer make it available as extruded sheets, casts or blown films, and injection or blow molded finished articles. It is widely used in several applications, including medical devices, packaging films, cosmetics containers, and microfluidics. Moreover, this copolymer's high glass transition temperature (up to 180°C) and high heat distortion temperature (about 170°C) make it appropriate low-cost substituent for polycarbonates (PCs) [2].

Also, the effective thermal radiation shielding of poly (ethylene-co-norbornene) based COC foams may open new perspectives in the fabrication of thermal insulation foams [37].

Hydrogenated polynorbornenes as cyclic olefin polymers (COPs) were commercialized since 1990's and have found increasing applications in pharmaceutical

syringes and vials thanks to their superior properties vs. glass and other transparent thermoplastics. This engineering thermoplastic was synthesized via ROMP of norbornene using Grubb's catalyst and subsequent in situ hydrogenation [38].

Low protein adsorption, outstanding moisture barrier, extremely low extractable, considerable fracture resistance, and transparency make hydrogenated polynorbornene an excellent choice for prefilled syringes and vials suitable for parenteral and lyophilized biopharmaceuticals. Also, the low fluorescence, high optical transmission, low haze, and precise mouldability of such COPs make them great selections for bio-diagnostic and life-science devices. The other advantages of this polymer include low risk of interaction with drug and excellent container closure integrity (CCI) at cryogenic temperatures (polymer/rubber thermal expansion coefficients match). However other candidates suffer from limitations in one or more ways. For instance, despite the extreme resistance of poly (vinylidene chloride) to oxygen and water, its sterilization results in HCl release, which causes compatibility issues.

On the other side, the superior dimensional and optical stability of COPs, even after prolonged exposure to high humidity and heat, are beneficial options for mobile devices and large-format TVs (LCDs and OLEDs). Also, displays with excellent viewing angles can be made from COPs, due to their stable, uniform birefringence even at sharp, oblique viewing angles from any seat [39–42].

Unlike the aforementioned cyclic olefin (co)polymers, Poly dicyclopentadiene (PDCPD) is a thermoset with potential and typical applications in transportation system components such as vehicles' body panels' (cabin roof, floor, engine bonnets, mudguards), agriculture equipments, chemical and wastewater treatment, and renewable energy production (wind turbine blades). PDCPD produced by polymerization of low viscosity dicyclopentadiene using Grubb's catalyst through a ring-opening metathesis approach. It is a successful alternative for metals and ceramics in various durable articles and heavy-duty applications [2].

Recently the degradability and recyclability of thermosets like PDCPD has been investigated. It has been shown that the incorporation of some cleavable bonds within the polymer chains, facilitates the triggered degradation of such thermoset material [43].

Hydrogenated poly(1,3-cyclopentadiene) (HPCPD) is synthesized through ROMP of DCPD, followed by the double bond hydrogenation. It is a low molecular weight polymer soluble in volatile and non-volatile hydrocarbons that imparts water-proof characteristics to the formulations and adhesion [16]. HPCPD with low risk of carcinogenicity, toxicity, and allergies is used in several applications, including cosmetics (e.g., film formers, waterproofing agents and blends combinations), creams, lotions, gels, hair, skin and sun care [44–46].

For the first time, **syndiotactic polystyrene (sPS)** has been developed in Idemitsu Kosan Central Research Laboratory. It was synthesized using single-site cyclopentadienyl titanium trichloride-based metallocene catalysts in the presence of methyl aluminoxane as cocatalyst [47]. Syndiotactic polystyrene is currently available as XAREC™, which is a superior environmentally friendly engineering thermoplastic. It has a high melting point (270°C) compared to its isotactic analogue (240°C). More importantly, the crystallization rate of sPS is 40 to 80 times higher than iPS at the same cooling conditions. The high heat distortion temperature, excellent chemical resistance, dielectric constant, and dissipation factor are of the primary advantages of this engineering polymer.

sPS is utilized in temperature resistant automotive and home appliance applications and its biaxially oriented film is used in high-temperature resistant films, e.g., ovenable packaging. However, to overcome its inherent brittleness and poor impact

strength, nanocomposites of sPS reinforced with glass or carbon fibers, mineral fillers or elastomers are developed [48].

Owing to the excellent thermal, electrical and chemical resistance, low specific density, and being environmentally friendly, sPS is prospective in the fabrication of electronic components of hybrid electric vehicles [49].

Styrene-diene (butadiene or isoprene) copolymers are synthesized via anionic polymerization, usually using butyllithium. **Hydrogenated styrene-diene (HSD) copolymers** are used as VI and classified into linear block and star copolymers. HSD block copolymers are synthesized via a step-by-step approach. The blocks are synthesized alternatively, i.e., the first block is synthesized and then the second block is added to the “living” polymer. Star-shaped HSDs are also synthesized in two steps. Generally, the core compound is one of divinylbenzene, polyhalogenated hydrocarbons, cyclosiloxanes, or calixarenes. The arms are di- or triblock copolymers of styrene, isoprene, or butadiene, which are grown from the reactive sites on the core [50].

The amorphous nature of HSDs affects the low-temperature flow characteristics. Such di-block copolymers and the associated micelles are efficiently used to improve the oil thickness at higher temperatures (100–150°C). HSDs are mainly utilized in high-performance motor oils for gasoline and diesel engines. Moreover, HSDs will find new applications in top-tier niches thanks to the ease of design of such block copolymers with specific topologies to have specialized features [27].

4.3 Functional polyolefins

Alternative olefin-carbon monoxide copolymers are tough semi-crystalline high-performance thermoplastics synthesized by coordination polymerization using late transition metal catalysts. This copolymer has been commercialized since the late 1990s, and now available as Poketone™ copolymer (ethylene-CO) and terpolymer (ethylene-propylene-CO) produced by Hyosung Chemicals.

Unique engineering properties such as exceptional impact and wear resistance, chemical and fuel resistance, gas barrier properties, and superior ductility over a broad temperature range are the significant advantages of this engineering thermoplastic.

Olefin-CO copolymers possess 2–3 times higher impact strength than polyamide (PA) and polybutylene terephthalate (PBT), higher hydrolysis resistance than PA, and better wear resistance than polyoxymethylene (POM). This thermoplastic is applicable in reinforced thermoplastic pipes (RTP) due to its high gas and hydrocarbon barrier properties. Moreover, its considerable resistance to automotive fluids made it a good candidate for application in the fuel system. Also, since this thermoplastic is safe with low to zero volatile compounds emission, it is used in food contact packaging, toys, and medical devices [51].

Generally, since the microstructural features of olefin-CO copolymers are translated into their macroscopic properties, a detailed understanding of the polymerization mechanism and structure-properties relationships is the key to design and synthesize new olefin-CO copolymers for specific applications. According to the literature, it seems that functional olefin-CO copolymers may find considerable attention in the future. The keto groups in olefin-CO copolymers may act as chemical “hooks” for anchoring the functional groups or crosslinking and curing the olefin-CO article after the processing [52].

The other perspective is incorporating a low amount of in-chain keto groups to render photodegradable polyethylene as an environmentally friendly sustainable thermoplastic while retaining its characteristic properties [53, 54].

Ethylene-Silicone block copolymers are novel block polymers in which ethylene and silicone units are covalently bonded together, using an appropriate catalyst system.

In 2018, the Chemical Society of Japan Award for Technical Development was given to Mitsui Chemicals for Exfola™ (first commercial ethylene-Si block copolymer) production and commercialization.

This functional polyolefin is an additive that combines the characteristics of polyolefin and silicone. So, the surface properties of polyolefins (i.e., release properties, water and oil repellency, coefficient of friction, abrasion resistance, and surface smoothness) are affected by such surface modifier, especially in injection molded or extruded articles, sheets, and films. In other words, this functional olefin-based copolymer changes the surface of a molded polyolefin article to silicon-specific characteristics by adding a small amount of this surface modifier during the molding process [55].

Lotryl® MA and Lotryl® BA (SK Chemicals), Optema™ and EnBA (ExxonMobil), and EMAC® and EBAC® (westlake), all are **ethylene-methyl (or butyl) acrylate copolymers (EA)** produced by high-pressure high-temperature radical polymerization, with acrylate content of up to 40 wt%. By increasing the acrylate content, the adhesion, solubility, toughness, compatibility with polar substrates, filler acceptance, and flexibility of the copolymer are enhanced. At the same time, the crystallinity, melting point, softening point, rigidity, and hardness are decreased [56].

Thanks to their outstanding compatibility with other thermoplastics and materials besides superior adhesive properties, EA copolymers are used as impact modifiers in engineering plastics (PET, PBT), base materials for filled compounds (masterbatches, wire and cables), and sealable films and layers in flexible packaging. For example, the application of this copolymer in hot melt adhesive composition, relates to its high compatibility with other polymers and raw materials such as tackifiers, waxes, and plasticizers [57].

Although EA copolymers are widely used in several applications, the harsh radical polymerization conditions (pressure range of 250–3000 bar and temperature range of 150–375°C) lead to a poor control over the microstructure, i.e., broad molecular weight and comonomer composition distributions. Therefore, the synthesis of tailor-made polar copolymers of ethylene under mild conditions, using coordination insertion polymerization and controlled radical polymerization approaches gained much attention in the last years. Well-defined functional polyolefins with controlled architectures and topologies will increase the versatility of such copolymers and opens new horizons in polyolefin niche applications [58, 59].

The introduction of acid side branches into the polyolefin substrate brings unique functionalities to **ethylene-acrylic acid copolymers (EAA)**. The acrylic acid units enhance its adhesion to polar substrates including papers, aluminum foil, metallized films, iron, steel, glass, ionomers and polar polymers (e.g., PA and poly ethylene-co-vinyl acetate (EVA)), significantly.

Escor™ and Nucrel™ are commercially available ethylene-acrylic acid copolymers (6–11 wt% AA), produced by ExxonMobil and Dow Chemicals, respectively.

Unlike conventional chemical primers and adhesive solutions, EAA copolymers provide excellent high-speed extrusion coating and lamination without the need to inconvenient and rate-limiting adhesive application and drying. So, EAA copolymers are cost-effective solutions for foil adhesion. Strong bonds form between EAA and the oxide layer on the aluminum that is highly resistant against mild to moderate acidic or basic environments.

Moreover, Nucrel™ AE is a specialized ethylene-methacrylic acid-acrylate terpolymer (EMAA), providing improved foil adhesion and enhanced hot tack strength [60].

Unistole™ is a liquid thermoplastic, commercially available as **hydroxyl- or acid-modified polyolefin**. It is utilized as non-chlorine, colorable, primer, or adhesive compatible with almost all types of paints, used in the automotive industry, medical packaging, printing materials, bonding agents, and tackifiers besides high-performance packaging. It has superior adhesion to a wide variety of polar substrates, such as Nylon 6, polyurethane, PBT, ABS, and EVA, flexibility and heat-seal properties.

Surlyn® is a smart intrinsic self-healing thermoplastic based on **partially neutralized** (with Na⁺, Mg⁺ or Zn⁺ ion) **ethylene-(meth) acrylic acid copolymer** synthesized via high pressure free radical polymerization using tubular reactors by Dow Chemical Company.

This ionomer enables microcrack repairment under specific triggers. Accordingly it is majorly utilized in impact protection applications such as golf balls, boats, or car bumpers [61]. Moreover, its potential application in hypervelocity impact-resistant less vulnerable spacecraft protecting bumpers against space debris has been evaluated, recently [62].

In addition, this clear, adjustable, and cost-effective engineering thermoplastic resin is utilized in packaging applications due to its excellent barrier properties and resistance to oil penetration. Also, besides the polar units within the polyolefin chain, the low sealing temperature of this ionomer makes it a good choice for adhesives and tie-layer materials. Moreover, considering the superior puncture, tear, and abrasion resistance of this ionomer, its significant applications include coatings, inks, food packaging, sporting goods, and cosmetics molded containers. The excellent heat sealability and oil and grease resistance provided by EAA ionomers make composite films gain popularity in the food packaging industry and rise in demand for such films.

Since poly (ethylene-co-methacrylic acid) metal composites exhibit flexibilities like traditional ionic polymer metal composites (IMPCs), they are considered as promising candidates for novel soft robotic actuators and sensors utilized in finger joints, hip, knee, or segmented limbs as well as energy harvesters [63].

Electrochromic devices (ECDs), such as chromogenic windows in aircraft, automobiles and buildings, are attractive potential applications of electrochromic materials both from the academic and industrial points of view for their selective and controlled visible light and solar energy transmission. Gelatin-based electrolyte films blended with EAA copolymer have demonstrated improved coloration efficiency compared to ones prepared by the solution mixing technique. This solvent-free approach will increase the chance of gelatin-based ECDs early commercialization [64].

Ethylene-vinyl acetate copolymers (EVA) are specialty thermoplastics produced via radical polymerization and commercially available with vinyl acetate content of 15 to 45 wt% or even more [65, 66].

EVA is an intelligent choice for flexible, puncture-resistant, and low seal initiation temperature (means faster packaging speeds) food and medical packaging which is a suitable replacement for PVC in non-invasive medical tubing and bag applications. Moreover, thanks to its good flow in the heat seal process and excellent crack resistance, EVA is suitable for block cheese, cereal, snacks, and fresh meat packaging. On the other side, most of the caps, closures and lids are made from EVA due to its good gas permeability, sealability, and heat resistance [60]. Also, EVA is used in automotive seals, for example, rocker head covers, due to its long-term heat stability besides good resistance to automotive fluids [67].

Recently, the low potential induced degradation (PID) and high transparency of new qualified grades of EVA made them promising for encapsulant sheet materials in photovoltaic cells [68].

SPO	Trade Name	Manufacturer	Functionality	Applications
PB	Akoafloor Akoalit Koattro Toppyl Purell	Lyondell Basell	—	easy-open packaging, film modification, hot melt adhesives, polyolefin modification, hot-water tanks, pipe and fittings, shoe sole
PMP	TPX™	Mitsui Chemicals	—	semiconductors, wires and cables, medical packaging, food packaging, films, household
PDCPD	Metton® LMR	Metton America	—	large truck and service vehicle body panels, construction parts, shipping containers, fan shrouds, septic and water treatment equipment, engine covers and fenders, hoods, bonnets
	Telene®	Telene RIMTEC Corporation		
sPS	Xarec	Idemitsu	—	automotive cooling applications automotive high voltage applications, plating grade, circuit boards, LED, food contact and potable water
EPDM	Dutral	Versalis	—	“sponge” profiles for cars, weather-sealings, building profiles, wire & cables, washing machine gaskets, home appliances, automotive interiors, automotive plastics modifiers, single-ply roofing, belts, O-rings, grummets, hoses, radiator-hose, diaphragms, accumulator bladders, geo-membranes
	Nordel	Daw Chemicals		
	Esprene™	Sumitomo		
	Keltan®	Lanxess		
	KEP	Kumho Polychem		
	Vistalon™	ExxonMobil Chemical		
COC	Topas®	Topas Advanced Polymers	—	perfect parenteral packaging, wearables, drug delivery, medical devices, recycle-friendly shrink labels & films, protective packaging, films, easy tear packaging, cellophane-like twist films, cosmetics and bottles, microplates, antennas for mobile devices
	Apel™	Mitsui Chemicals		
	Arton	JSR Corporation		
COP	Zeonex® Zeonor®	Zeon Corporation	—	pre-filled drug delivery devices (syringes and cartridges), vials and bottles for long-term biological materials storage, IV and total parental nutrition (TPN) bags, bio-reactors, high-pressure injection syringes (needle-free, viscose drug and large dosage injection), autoinjectors, cells for hem analysis, lenses, prisms, sunglass-friendly touch sensors, optical films and sheets for LCD and OLED displays, optical fibers, optical lenses in digital cameras and laser beam printers

SPO	Trade Name	Manufacturer	Functionality	Applications
HPCPD	Koboguard®	Kobo Products	—	cosmetics (film formers, substantivity agents, waterproofing agents, blends combinations, sunscreen agents, lubricants slip agents, dispersants), creams, lotions and gels, decorative cosmetics and makeup, hair care (shampoos, conditioners and styling), skincare (facial care, facial cleaning, bode and baby care), sun care (sun protection, after-sun and self-tanning), lipsticks, concealer, lip balm with SPF, blush, lip gloss, bronzers, highlighters, brow liner, eye shadow, lip balm, foundation, eyeliner
TOR	Vestenamer®	Evonik	—	tires (strips, apex, tread, sidewall, recycling, bladders), rubber recycling (virgin rubber blends, rubber-modified asphalt, recycling rubber goods), rubber goods (hoses, profiles, seals, rolls, drive belts, conveyor belts, cable and wires, flooring and roofing, molded goods, foamed products), medicals (rubber stoppers, thermoformable products), sports (golf balls), shoe soles, masterbatches (additives, carbon, Sulfur), thermoplastics
HPD	PAO 4 FG	Chevron Philips	—	cosmetics primary and secondary oils (as carrier and moisturizers), glazing or polishing agent for dried fruits and particular sugar confectionery (e.g., fruit gums and jellies), substituent for white mineral oil, release ('non-stick') coating in bread tins, lubricant in dough-dividing machines, anti-dusting and anti-foaming agent, plasticizer in food contact films
PEC	Vistamaxx™	ExxonMobil Chemicals	—	hot melt adhesives, sealing layer in co-extruded articles, masterbatch formulations, compound modification, stay-flat carpet tiles, breathable soft-stretch elastic nonwoven fabrics
OCP	HiTEC®	Afton Chemicals	—	VI for automotive and industrial applications (engine oils, hydraulic fluids, tractor fluids, wireline, gear oils, grease)
	Paratone	Chevron Oronite		
	Nordel IP	Dow Chemicals		
	Lubrizol	Lubrizol		
	Viscoplex	Evonik		
	Dutral Co	Versalis		
E-Si	Exfol	Mitsui Chemicals	Silicone	surface modifier of polyolefin films, sheets, containers, and packages

SPO	Trade Name	Manufacturer	Functionality	Applications
E-CO	Poketone	Hyosung Chemicals	ketone	toys, sporting goods, food contact parts (food packaging films, water purifiers, faucets), cosmetic packaging, dispensing solutions packaging, pipes (downhole pipe liners, tubes, fitting, filaments), automotive (connectors, worm wheel hubs/gears, fuel system), medical (nasal sprays, snap-fits, valves, nozzles, surgical instruments, technical disposals), gear (glove conveyors, ATM gears, Helmet parts for motors and bikes, refrigerator rotor), electronics (mobile bracket, connector housing, Watt-hour meter), Industrial (rail fastening system, caster)
EA	Emac® Ebac®	Westlake Chemical Corporation	methyl acrylate butyl acrylate	hot melt adhesives, wire and cable, masterbatches, extrusion coated structures, extruded laminates, hot melt adhesives for deep-freeze packaging, sealable layer for food packaging, films, impact modification of engineering plastics
	Lotryl® MA Lotryl® BA	SK Functional Polymer		
	Optema™ EnBA	ExxonMobil Chemicals		
	Acryft®	Sumitomo Chemicals		
EAA	Escor™	ExxonMobil Chemicals	acrylic acid	adhesives, sealants, coatings, laminates, tube containers, transparent packaging, packaging (condiments, juices, aseptic milk, personal care products, pharmaceuticals), cable shielding, metallized building panels, water piping
	Nucrel™	Dow Chemicals		
EAA ionomer	Surlyn	DuPont	neutral acrylic acid	coatings, inks, surface coating films for golf balls, food packaging, sports equipment, molded bottles of cosmetics, medical device packaging, stretch packaging, packaging of food materials such as meat, poultry, fish, seafood, cheese, edible oil, vegetables, flexible packaging formats such as sachets, pillow pouches, flow-wrap packages, anti-corrosion paints, composite cans
	Chemipearl™	Mitsi Chemicals		

SPO	Trade Name	Manufacturer	Functionality	Applications
EVA	Escorene™	ExxonMobil Chemicals	vinyl acetate	gauge films, bags, pouches, carpet backing, film wrap, lamination film, sealants, sealants in meat, dairy packaging structures, footwear, wire and cable insulation, photovoltaic encapsulants and sheets, packaging (block cheese, cereal and snacks, fresh meat barrier packaging, closures, lids) films, medical packaging, footwear, hot melt adhesive, ink, road bitumen modification, heat seal agent for paper, film and aluminum foil in packaging chocolate and confectionery, anti-blocking agents, greenhouse covers, hot melt adhesives in book-binding, modification of emulsions
	Elvax™	Dow Chemicals		
	Sumitate®	Sumitomo		
	Evatane®	SK Chemicals		
	Ultrathene	Lyondell Basell		
	Levapren®	Arlanxeo		
	Chemipearl™	Mitsui Chemicals		
	Elevate®	Westlake chemicals		
EVMA	Orevac® T	SK functional polymers	vinyl acetate-maleic anhydride	flexible packaging, multilayer blown films and cast films, shrinkable films, barrier lidding films, vacuum bags, coextruded multilayer barrier and composite pipes, multilayer tubes and pipes, pipe coating, heat shrinkable sleeves, automotive industry (door panels, seats and roofing, bonding of textile substrates in seats covers and headliners), carpets, sound proofing, heat insulation materials, sports and leisure (skis, sails, shoes (textile uppers, liners)), furniture (decorative films, mattresses, seats, wall covering, bonding of foams on woven and non-woven), shrinkable bags, lids for trays, tubular films
KEE	Elvaloy™	Dow	ketone-ester	ready-to-eat meal packaging, asphalt paving, cable jacketing, roofing membranes, PVC and other plastics modification

Table 1.
Function-application review of commercially available specialty polyolefins (SPO).

Random terpolymers of ethylene-vinyl acetate-maleic anhydride (EVAMAH) are manufactured by the high-pressure radical polymerization process. They are commercially available as Orevac[®] T. A transparent, flexible, soft, and reactive polyolefin-based functional thermoplastic with superior adhesive properties to several polar and non-polar substrates, generally utilized as tie-layer in multilayer films, tubes, and pipes. It is used to bond diverse solid substrates such as PA, PU, and PET films, metallic foils, fiber glass fabrics, textiles, artificial leather, natural fibers, wood, and foams.

While vinyl acetate units provide softness, flexibility, and polarity to this terpolymer, maleic anhydride gives reactivity to Orevac[®] T, leads to adhesive properties far better than EVA copolymers [69].

Ketone-Ethylene-Ester (KEE) terpolymers are commercially available as Elvaloy[™] provided by Dow Chemicals. KEE improves the durability, flexibility and long-lasting characteristics of other resins. In addition, when combined with PET, it provides desired level of low-temperature toughness, especially in refrigerated and frozen meals.

Moreover, KEE terpolymers modify the long-term properties and load carrying capacity of asphalt as polymeric modifiers. Also, the permanent flexibility, high cutting, puncture, shrinkage, and chemical resistance of Evaloy/PVC compounds made them the most durable, fastest to install, and most accessible to repair, high-performance single-ply PVC roofing [60].

A list of the specialty polyolefins which has been reviewed in this chapter, is given in **Table 1**. The trade name, manufacturer, Functionality added to the polyolefin chains, and applications of such specialties are summarized.

5. Challenges in the commercialization of functional polyolefins

Since the early 2000s, the synthesis of functional polyolefins with complex architectures faced tremendous progress thanks to the development of novel insertion polymerization catalysts enabling the synthesis of polyolefins with highly controlled molecular weight, chemical composition distribution, and topology. The precise synthesis of functional polyolefins opens up new windows toward the development of engineering grades based on structure–function relationships [10].

Undoubtedly, catalytic polymerization will stand at the core of functional polyolefin production. However, the remaining related challenges are as below;

- The environmental concerns, including polyolefins accumulation in the environment, are perhaps essential challenges. Some of the potential solutions are the production of biodegradable polyolefins, increasing their recyclability, and developing new functional polyolefins as replacements for non-olefin based materials to reduce the sorting requirement during recycling. The other potential approach is the catalytic depolymerization or upcycling of polyolefins through which valuable materials are obtained.
- The residual catalyst remains in the polyolefin matrix is another concern, not only from the toxicity point of view but also due to the undesirable degradation reactions acceleration in the presence of metallic contaminants. Also it is a substantial issue that may affect the polyolefins' recyclability and limits their applications. The most probable approach to solve this problem is developing super active catalysts capable of producing special-purpose functional polyolefins, e.g., with pendant antioxidant groups to suppress the undesirable degradation reactions during the service period [10, 70, 71]

Although random functional polyolefins are obtained by applying minimum changes compared to their corresponding homo-polyolefins, they offer drastically different chemical, physical, and surface properties. Therefore, random functional polyolefins are excellent candidates for the replacement of engineering thermoplastics, opening new windows toward the progression of new engineering polyolefins. However, despite the recent developments in the synthesis of such functional polyolefins, there are still several challenges in their production include;

- The active catalytic centers of highly exophilic early transition metal catalysts are deactivated by forming strong σ -coordination with the Lewis basic moiety of heteroatom-containing polar monomer. Accordingly, the late transition metal catalysts were introduced as promising substituents because they are more tolerant toward functional groups [12].

- The other major challenge originates from the relative electron deficiency of functional monomers compared to olefins, which results in the former lose-out during the competitive coordination to the metal center or perhaps stable chelates formation. Therefore, the poor π -donating ability of polar monomers avoids the formation of heteroatom-rich functional polyolefins.

Also, it still suffers from the limited coordination and insertion of the polar functional groups and vast imperfections in the synthesis of well-defined tailor-made functional copolymers [11, 70].

As a solution, the design of new catalysts capable of producing high polar comonomer content functional polyolefins seems to gain more potential in the future. However, despite the tremendous developments in highly effective olefin (co)-polymerization catalysts, only a few of these catalysts have found general applications in industrial polyolefin processes. There are a number of parameters that need to be evaluated. The parameters are catalyst activity and kinetics, range of products with a specific MW and MWD, morphology, branching density and comonomer incorporation homogeneity, tolerance toward polar monomers in the production of functional olefin copolymers as well as polymerization process economics and environmental issues [4, 11].

Also, chain-end functionalized polyolefins synthesized via chain-transfer reactions taking advantage of almost quantitative incorporation of the functional groups at the chain ends. This class of functional polyolefins is a superior starting point for the grafting from or block copolymer synthesis, where the functional fragments are created by another reaction mechanism successively. Furthermore, the complexity in controlling the microstructure and composition of functional copolymers encouraged the researchers toward the copolymerization of ethylene with dormant reactive comonomers. The dormant moiety transformed to functional groups through post-functionalization approaches or to initiators for graft-from polymerization of polar monomers [5].

The other approach comprises the precise synthesis of random functional polyolefins through metathesis polymerization.

Moreover, different synthetic pathways, such as functionalized carbenes as alternatives for the synthesis of functional polar monomers, are constantly developing [11].

- Last but not least is related to the development of functional polypropylenes. The lower reactivity of propylene compared to ethylene makes the production of functional propylene copolymers much more difficult than ethylene copolymers [72].

6. Trends in the specialty polyolefins industry

Specialty polyolefins growing in the last decade was faster than the past thanks to developing new catalytic systems and polymerization processes.

Nowadays, the possibilities in the synthesis of specialty polyolefins include;

- Homo-, co- and terpolymerization of olefins, dienes (as dormant sites for post-polymerization modifications), and polar vinyl monomers
- Stereospecific polymerization for the synthesis of all kinds of tacticities such as stereo-block, iso-block, semi-isotactic, syndiotactic, and atactic structures with tunable block lengths
- Strategies to control the topology of polyolefins, such as chain walking polymerization. Using late transition metal catalysts, a wide range of engineered polyolefins of complex chain architectures can be designed through the control of ligands' steric and electronic parameters [73–75].

The progress in specialty polyolefins production will help redefining polyolefins' intrinsic properties such as tackiness, biodegradability and sustainability [4]. Therefore, the future possibilities in specialty polyolefins production will be as follows;

- Controlled introduction of branches with tunable lengths
- Production of polyolefins with defined tacticities of prochiral monomers in the backbone
- Tailored co- and terpolymers with defined sequence and combination of monomers and topology. Examples include telechelic, comb-like, star, miktoarm, dendritic, and hyperbranched functional polyolefins or 3-D structures with self-organizing helix or zig-zag units, rigid or elastic blocks, and more sophisticated systems [76, 77].
- Multiblock polyolefins synthesized in the presence of chain shuttling agents
- Functional polyolefins obtained via hybrid insertion/radical polymerization
- In situ polyolefin nano- or micro-composites
- Polyolefin-based nano-catalysts, nanoreactors, and nanomachines taking advantage of the polyolefin conformational switch under various triggers according to the functionality and topology. The nanoreactors provide desired reaction conditions by allowing only suitable reactants to reach the embedded catalyst elements

Moreover, due to the emerging role of single-site catalysts in the development of specialty and functional polyolefins, the future trends in catalyst progression are listed as below;

- Production of new catalytic systems for the homo- and copolymerization of heteroatom-containing monomers capable of chain configuration regulation
- Inexpensive and straightforward activators to increase the catalyst activity several folds

- Highly active single-site catalysts for the industrial production of polypropylene with competitive cost, specific properties (e.g., elastomeric) and stereoregularity compared to the latest generation of Ziegler-Natta catalysts
- Simple, economical, and well-controlled approaches for the production of in-reactor polymer alloys by mixed catalysts
- New REACH and FDA approved catalytic systems
- Single-site catalytic systems producing polyolefins with enhanced processability

7. Conclusion

Olefins are cost-effective, highly available platforms for the development of functional polyolefins extending the alkenes' value chain. In this chapter, we have discussed how specialty polyolefins are finding their way in niche markets and their potential in shaping future applications. Moreover, the trends and challenges in the production of functional polyolefins are reviewed. Although this class of thermoplastics are synthesized using radical polymerization, at present, the poor control over the microstructural characteristics may boost the insertion polymerization application. Single-site catalysts will be the core in the progression of novel tailor-made functional polyolefins.

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