# Lecture Thirteen

# POLYPROPYLENE

Polypropylene (PP) is a major thermoplastic polymer. Although polypropylene did not take its position among the large volume polymers until fairly recently, it is currently the third largest thermoplastic after PVC. The delay in polypropylene development may be attributed to technical reasons related to its polymerization. Polypropylene produced by free radical initiation is mainly the atactic form. Due to its low crystallinity, it is not suitable for thermoplastic or fiber use. The turning point in polypropylene production was the development of a Ziegler-type catalyst to produce the stereoregular form (isotactic).

Catalysts developed in the titanium-aluminum alkyl family are highly reactive and stereoselective. Very small amounts of the catalyst are needed to achieve polymerization (one gram catalyst/300,000 grams polymer). Consequently, the catalyst entrained in the polymer is very small, and the catalyst removal step is eliminated in many new processes.

A new gas-phase process called "absolute gas phase" has been introduced in which polymerization of olefins (ethylene, propylene) occurs in the total absence of inert solvents such as liquefied propylene in the reactor. Titanium residues resulting from the catalyst are less than 1 ppm, and aluminum residues are less than those from previous catalysts used in this application.

Polypropylene could be produced in a liquid or in a gas-phase process.

Until 1980, the vertically stirred bed process was the only large-scale commercial gas phase process. In gas phase process (Figure 12-2), a wide range of polypropylenes are made in a fluidized bed gas phase reactor. Melt index, atactic level, and molecular weight distribution are controlled by selecting the proper catalyst, adjusting operating conditions, and adding molecular weight control agents. This process is a modification of the polyethylene process (discussed before), but a second reactor is added. Homopolymers and random copolymers are produced in the first reactor, which operates at approximately 70°C and 35 atmospheres. Impact copolymers are produced in the second reactor (impact reactor) after transferring the polypropylene resin from the first reactor. Gaseous propylene and ethylene are fed to the impact reactor to produce the polymers' rubber phase. Operation of the impact reactor is similar to the initial one, but the second operates at lower pressure (approximately 17 atmospheres). The granular product is finally pelletized.

Random copolymers made by copolymerizing equal amounts of ethylene and propylene are highly amorphous, and they have rubbery properties.


An example of the liquid-phase polymerization is the process in  (Figure 12-3), which uses a tubular reactor.
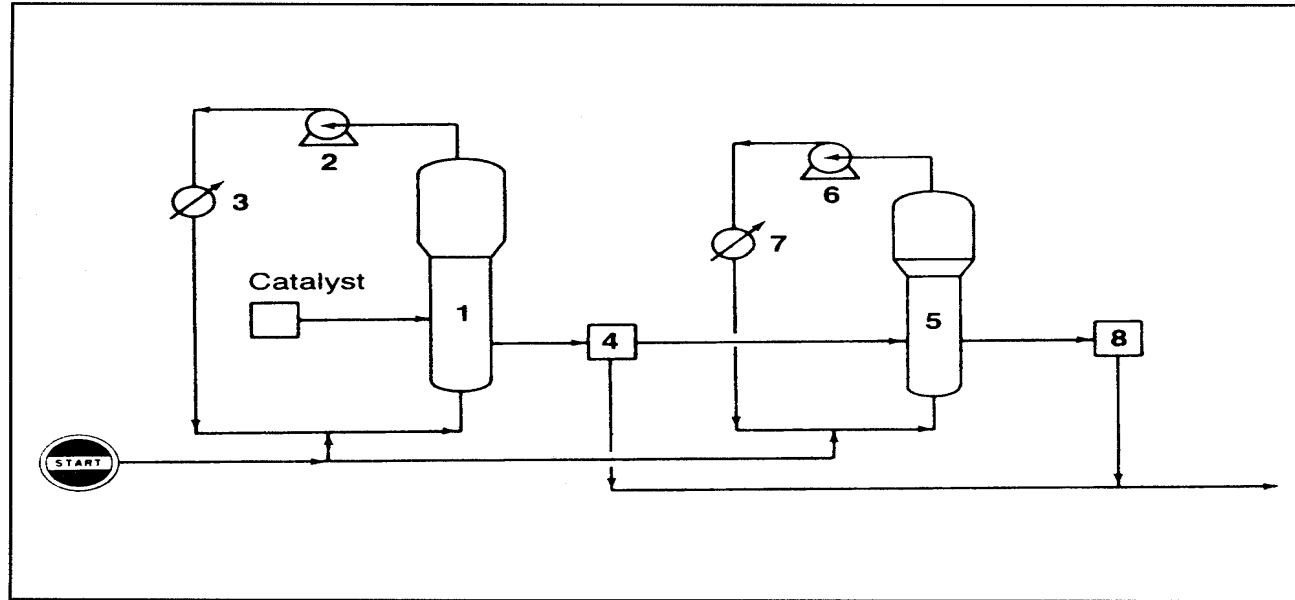
**Figure 12-2.** The Union Carbide gas-phase process for producing polypropylene: (1) reactor, (2) centrifugal compressor, (3) heat exchanger, (4) product dischargetank (unreacted gas separated from product), (5) impact reactor,(6)compressor,(7) heat exchanger,(8) discharge tank (copolymer separated fromreactedgas).
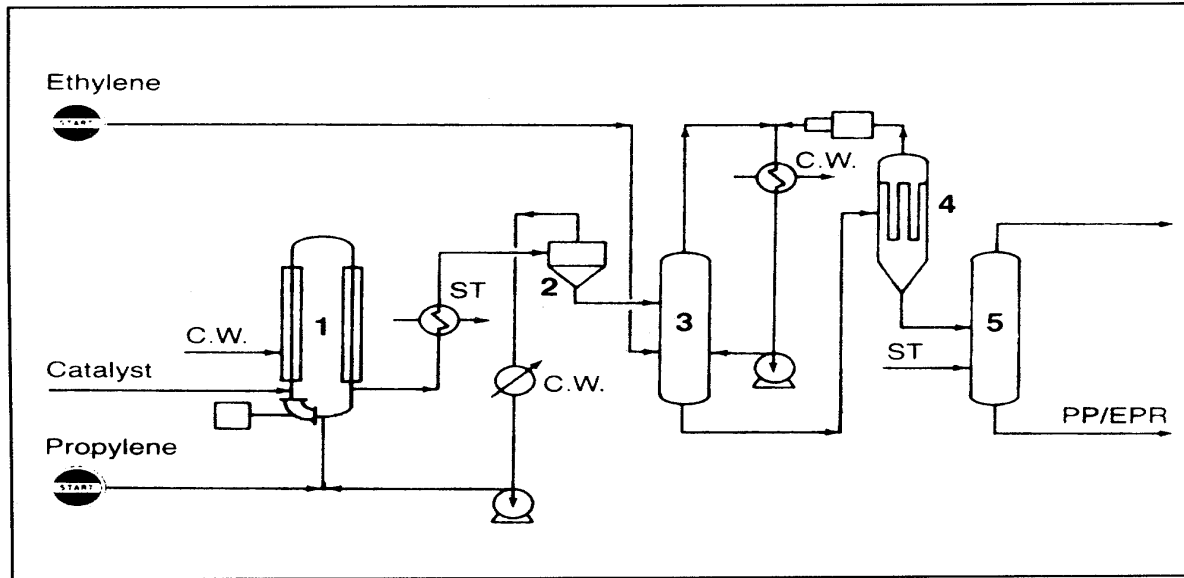
**Figure 12-3.** The Himont Inc. Spheripol process for producing polypropylene in a liquid-phase: (1) tubular reactor, (2,4) two-stage flash pressure system (to separate unreacted monomer for recycle), (3) heterophasic copolymerization gasphasereactor, (5) stripper.

Copolymerization occurs in a second gas phase reactor. Unreacted monomer is flashed in a two-stage pressure system and is recycled back to the reactor. Polymer yields of 30,000 or more Kg/Kg of supported catalyst are attainable, and catalyst residue removal from the polymer is not required. The product polymer has an isotactic index of 90–99%.

New generation metallocene catalysts can polymerize propylene in two different ways. Rigid chiral metallocene produce isotactic polypropylene whereas the achiral forms of the catalysts produce atactic polypropylene. The polymer microstructure is a function of the reaction conditions and the catalyst design.Recent work has shown that the rateof ligand rotation in some unbridged metallocenes can be controlled so that the metallocene oscillates between two stereochemical states. One isomer produces isotactic polypropylene and the other produces the atactic polymer. As a result, alternating blocks of rigid isotactic and flexible atactic polypropylene grow within the same polymer chain.

## Properties and Uses of Polypropylene

The properties of commercial polypropylene vary widely according to the percentage of crystalline isotactic polymer and the degree of polymerization. Polypropylenes with a 99% isotactic index are currentlyn produced.
Articles made from polypropylene have good electrical and chemical resistance and low water absorption. Its other useful characteristics are its light weight (lowest thermoplastic polymer density), high abrasion
resistance, dimensional stability, high impact strength, and no toxicity.
Table 12-3 shows the properties of polypropylene.

Polypropylene can be extruded into sheets and thermoformed by solid-phase pressure forming into thin-walled containers. Due to its light weight and toughness, polypropylene and its copolymers are extensively used in automobile parts.
Improvements in melt spinning techniques and film filament processes have made polypropylene accessible for fiber production. Low-cost fibers made from polypropylene are replacing those made from sisal and jute.
World demand for polypropylene is expected to be 30 billion pounds by 2002. This is the strongest growth forecast for any of the major thermoplastics (5.9%). Many of the resins new applications particularly in packaging come at the expense of PS and PVC, the two resins that have been the subject of regulatory restrictions related to solid waste issues and potential toxicity.

## Table 12-3
## Properties of polypropylene

| | |
|---|---|
| Density , g/cm$^3$ | 0.9-0.91 |
| Fill temperature , max. ºC | 130 |
| Tensile strength , psi | 3,200-5,000 |
| Water absorption , 24 hr,% | 0.01 |
| Elongation,% | 3-700 |
| Melting point , $T_m$ºC | 176 |
| Thermal expansion,10$^{-5}$ in/in. ºC | 5.8-10 |
| Specific volume,cm$^3$/lb | 30.4-30.8 |

**Polyvinyl Chloride**

$$\left[\text{CH}_2\text{—CH}\right]$$
$$\underset{\text{Cl}}{|}$$
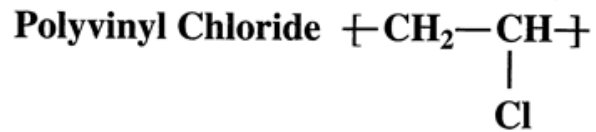
Polyvinyl chloride (PVC) is one of the most widely used thermoplastics. It can be extruded into sheets and film and blow molded into bottles. It is used in many common items such as garden hoses, shower curtains, irrigation pipes, and paint formulations.

PVC can be prepolymerized in bulk to approximately 7–8% conversion. It is then transferred to an autoclave where the particles are polymerized to a solid powder. Most vinyl chloride, however, is polymerizedin suspension reactors made of stainless steel or glass-lined. The peroxide used to initiate the reaction is dispersed in about twice its weight of water containing 0.01–1% of a stabilizer such as polyvinyl alcohol.

In the European Vinyls Corp. process (Figure 12-4), vinyl chloride monomer (VCM) is dispersed in water and then charged with the additives to the reactor.It is a stirred jacketed type ranging in size between 20–105m$^3$. The temperature is maintained between 53–70°C to obtain a polymer of a particular molecular weight. The heat of the reaction is controlled by cooling water in the jacket and by additional reflux condensers for large reactors.

Conversion could be controlled between 85–95% as required by the polymer grade. At the end of the reaction, the PVC and water slurry are channelled to a blow down vessel, from which part of unreacted monomer is recovered. The rest of the VCM is stripped, and the slurry is centrifuged to separate the polymer from both water and the initiator.

Polyvinyl chloride can also be produced in emulsion. Water is used as the emulsion medium. The particle size of the polymer is controlled using the proper conditions and emulsifier. Polymers produced by free radical initiators are highly branched with low crystallinity.

Vinyl chloride can be copolymerized with many other monomers to improve its properties. Examples of monomers used commercially are vinyl acetate, propylene, ethylene, and vinylidine chloride. The copolymer with ethylene or propylene ($T_g = 80°C$), which is rigid, is used for blow molding objects. Copolymers with 6–20% vinyl acetate ($T_g = 50–80°C$) are used for coatings.
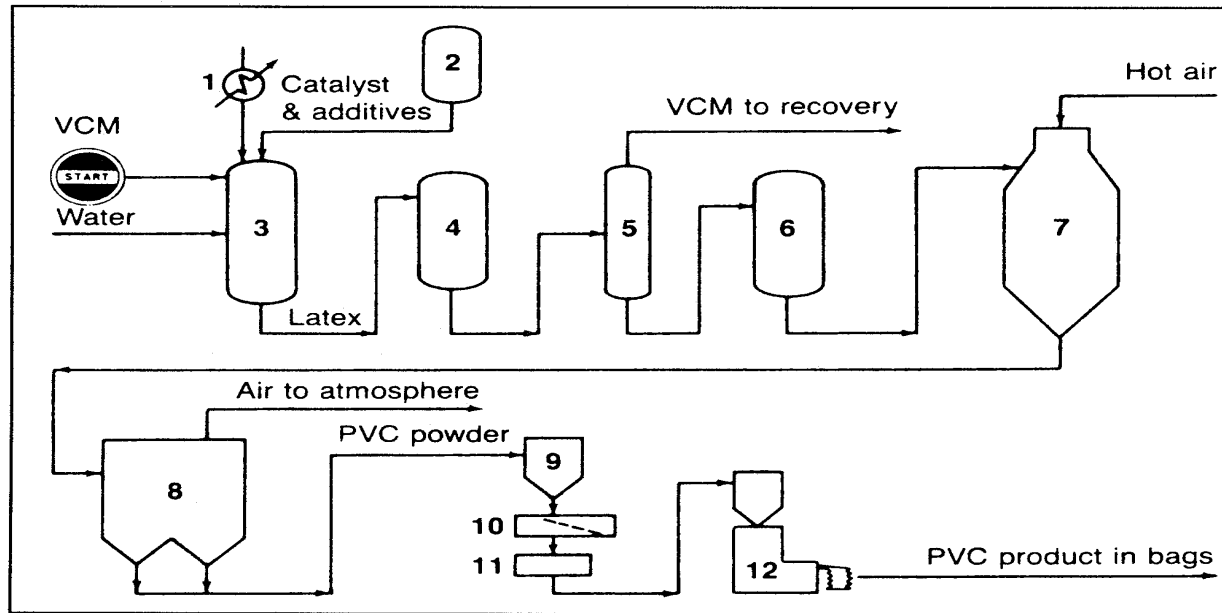
**Figure 12-4.** The European Vinyls Corp. process for producing polyvinyl chloride using suspension polymerization: (1) reactor, (2) blow-down vessels (to separate unreacted monomer), (3) stripping column, (4) reacted monomer recovery,(5)slurry centrifuge, (6) slurry drier.

## Properties and Uses of Polyvinyl Chloride

Two types of the homopolymer are available, the flexible and the rigid.

Both types have excellent chemical and abrasion resistance. The flexible types are produced with high porosity to permit plasticizer absorption. Articles made from the rigid type are hard and cannot be stretched more than 40% of their original length. An important property of PVC is that it is self-extinguishing due to presence of the chlorine atom.

Flexible PVC grades account for approximately 50% of PVC production. They go into such items as table cloths, shower curtains, furniture, automobile upholstery, and wire and cable insulation. Many additives are used with PVC polymers such as plasticizers, antioxidants, and impact modifiers. Heat stabilizers, which are particularly important with PVC resins, extend the useful life of the finished product.

Rigid PVC is used in many items such as pipes, fittings roofing, automobile parts, siding, and bottles.

The 1997 U.S. production of PVC and its copolymers was approximately 14 billion pounds.

# THERMOPLASTIC POLYESTERS

Thermoplastic polyesters are among the large-volume engineering thermoplastics produced by condensation polymerization of terephthalic acid with ethylene glycol or 1,4-butanediol. These materials are used to produce film for magnetic tapes due to their abrasion and chemical resistance, low water absorption, and low gas permeability.Polyethylene terephthalate (PET) is also used to make plastic bottles (approximately 25% of plastic bottles are made from PET). Similar to nylons, the most important use of PET is for producing synthetic fibers .

Polybutylene terephthalate (PBT) is another thermoplastic polyester produced by the condensation reaction of terephthalic acid and 1,4-butanediol:
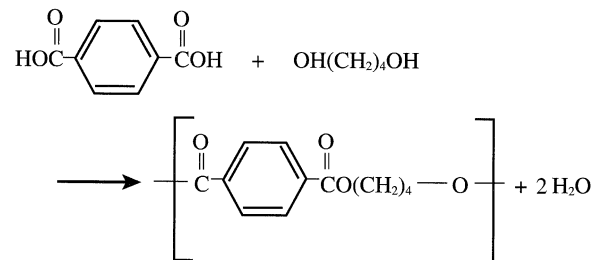
The polymer is either produced in a bulk or a solution process. It is among the fastest growing engineering thermoplastics, and leads the market of reinforced plastics with an annual growth rate of 7.3%.

The 1997 U.S. production of thermoplastic polyesters was approximately 4.3 billion pounds.

# SYNTHETIC FIBERS

Fibers are solid materials characterized by a high ratio of length to diameter. They can be manufactured from a natural origin such as silk, wool, and cotton, or derived from a natural fiber such as rayon. They may also be synthesized from certain monomers by polymerization (synthetic fibers). In general, polymers with high melting points, high crystallinity, and moderate thermal stability and tensile strengths are suitable for fiber production.

Man-made fibers include, in addition to synthetic fibers, those derived from cellulose (cotton, wood) but modified by chemical treatment such as rayon, cellophane, and cellulose acetate. These are sometimes termed "regenerated cellulose fibers." Rayon and cellophane have shorter chains than the original cellulose due to degradation by alkaline treatment. Cellulose acetates produced by reacting cellulose with acetic acid and modified or regenerated fibers are excluded from this book because they are derived from a plant source. Fibers produced by drawing metals or glass ($SiO_2$) such as glass wool are also excluded.

Major fiber-making polymers are those of polyesters, polyamides (nylons), polyacrylics, and polyolefins. Polyesters and polyamides are produced by step polymerization reactions, while polyacrylics and polyolefins are synthesized by chain-addition polymerization.