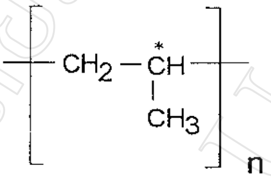
CHAPTER 2

POLYPROPYLENE

2.1 Polypropylene [13]

2.1.1 Chemical Structure

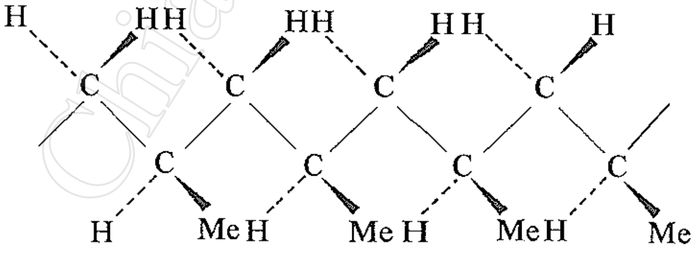
Structural Repeating Unit



$$\left[-CH_2-\overset{*}{C}H- \atop \quad\quad\ \ CH_3 \right]_n$$

C_3H_6 , mol. wt. = 42

In the structural repeating unit of polypropylene, as shown above, the $^{*}C$ atom is asymmetric. Commercial polymers are usually around 95% isotactic, i.e. stereoregular in structure, each repeat unit in a given chain being unidirectionally arranged and having the $-CH_3$ group in the same spatial configuration, as illustrated below:



—— = C-C bonds lying in the plane of the paper

◢ = bonds protruding ***above*** the plane of the paper

----- = bonds protruding ***below*** the plane of the paper

Me = the substituent methyl group, CH_3

The crystallinity and rigidity of the commercial isotactic polymer arise from this regularity of structure. The polymer is predominantly linear, although some chain branching is usually present.

2.1.2 General Characteristics

Polypropylene is a translucent thermoplastic material, somewhat resembling stiffened polyethylene but usually more glossy in appearance; it is also available as clear biaxially-oriented films and fibres. It has a high tensile strength and, compared with polyethylene, a higher softening temperature. It becomes brittle at only moderately low temperatures but is free from environmental stress cracking.

Polypropylene is used as a general purpose moulding material in plastics applications, while its films and fibres find use in packaging and textiles respectively.

2.1.3 Chemical Properties

Polypropylene, as a predominantly linear hydrocarbon containing little or no unsaturation, resembles polyethylene in several of its characteristics. However, the methyl groups, attached isotactically to alternate C-atoms in the molecular chain, modify the properties in certain ways, e.g. causing stiffening (which raises the glass transition temperature and the melting point) and rendering it less stable than polyethylene with regard to oxidation. In particular, the methyl groups lead to asymmetry and the possibility of obtaining products of different tacticity but it is the isotactic structure that is important in commercial polymers.

Solvents: polypropylene is dissolved only at elevated temperature by aromatic hydrocarbons (e.g. xylene, tetralin, decalin) and chlorinated hydrocarbons (e.g. chloroform, trichloroethylene) above 80°C.

Plasticised by elastomers (e.g. nitrile rubbers) and ester plasticisers (e.g. dioctyl phthalate) but best plasticised internally by copolymerisation.

Swollen by aromatic hydrocarbons (e.g. xylene) and chlorinated hydrocarbons (e.g. chloroform) at room temperature, also by esters (e.g. ethyl acetate, dibutyl or dioctyl phthalate), ethers (e.g. diethyl ether, tetrahydrofuran, dioxane) and by various aqueous oxidising agents (e.g. 10% HNO_3, 10% $KMnO_4$).

Relatively unaffected by many organic liquids at room temperature (e.g. alcohols, glycols) and aqueous solutions including moderately concentrated acids and alkalis (but less satisfactory above 60°C, especially with mild oxidising agents).

Decomposed by strong oxidising agents (e.g. HNO_3, chlorosulphonic acid) especially when warm (e.g. attacked by hot concentrated HNO_3); slowly weakened (e.g. fall in fibre strength) by concentrated alkali. Polypropylene is more readily oxidised than polyethylene, the rate of attack and range of reagents increasing with temperature.

2.1.4 Physical Properties

Specific gravity depends on the polymer's degree of crystallinity and usually varies within the range 0.89 - 0.91 [14]. Increase in density raises the softening temperature, stiffness and yield strength, but decreases permeability, low temperature brittleness, tensile strength, and extension at break.

Refractive index (η) 1.49.

Water absorption (discs 3 mm thick; wt. % in 24 h) 0.01-0.03. Increase in weight after 6 months in an aqueous environment: at 20°C, under 0.5%; at 60°C under 2%.

Moisture regain (percentage at 65% r.h.) 0.0-0.15.

Water retention 5%.

Physical effects of temperature. The softening and melting ranges are 145-150°C and 165-175°C respectively. The polymer is subject to oxidation at 100°C but, when suitably stabilised, the molten material is stable up to 250°C and does not decompose in full until over 300°C.

2.1.5 Fabrication

Processing follows closely that of polyethylene but polypropylene has certain special characteristics. The melt viscosity remains relatively high up to 230°C, then falls slowly with rise in temperature to 275°C, and thereafter falls off rapidly; thus, for moulding and extrusion, the preferred working range lies between 230-275°C.

Injection moulding. Temperatures between 230-260°C; pressures of 10000-20000 lbf/in^2; mould temperature 35-90°C.

Extrusion. Temperatures between 210-270°C. Cast films are extruded from a slot-die into water or onto a chill roll; clear films require to be extruded at 270-300°C.

Fibres are melt spun at temperatures up to 270°C, then hot drawn to 5-10 times their length; wet spinning and dry spinning from hot solution have also been used.

2.2 Polypropylene Fibres [15]

The discovery of stereospecific polymerisation in 1954 opened the way for polypropylene to join the ever-growing family of fibre-forming polymers. High molecular weight isotactic polypropylene was found to be a most suitable raw material for fibre formation. The advantages of polypropylene fibres are their low cost and light weight. Improvements in stabilization, coloration and texturing of this versatile fibre led to substantial volume growth in the 1970s, which continues today at an even higher rate owing to recent advances in fibre-forming and textile technology.

2.2.1 Manufacture

For many years, the primary technology employed for the manufacture of polypropylene filament was melt spinning, similar to the method employed for polyester and polyamide fibres. As explained in the previous Chapter 1, the molten polymer is extruded through a spinnerette under pressure after preliminary filtration and deaeration. The basic process of melt spinning was illustrated in Figure 1.3 on page 4. The production line shown in Fig. 2.1 is mainly used for the manufacture of monofilament from polypropylene.

2.2.2 Quenching

Polypropylene and most other linear polyolefins crystallize more rapidly than most other crystallizable polymers. Unlike polyester, which is normally amorphous as spun, the fibre morphology is fixed in the spinning process; this limits the range of properties in subsequent drawing and annealing operations. In a low crystallinity state, sometimes called the paracrystalline or smectic form, a large degree of local order still exists. It can be reached by rapid quenching, e.g, in a cold-water bath. The more common commercial practice is controlled air quenching in which the rate of cooling is controlled by the velocity and the temperature of the air. In quenching, the rate of cooling largely controls the crystalline texture that is obtained. Rapid, low temperature quenching retards crystallization; slower, relatively high temperature quenching permits more complete development of crystallites. The ability to undergo subsequent drawing and, consequently, the mechanical properties depend on the quenching process. The rapidly quenched fibre usually gives lower elongation and higher tenacity during subsequent draw. With a very rapid quench, the melt may not be able to relax fast enough to sustain drawdown, resulting in melt fracture. With a slow quench, the melt may totally relax, leading to ductile failure of the threadline.

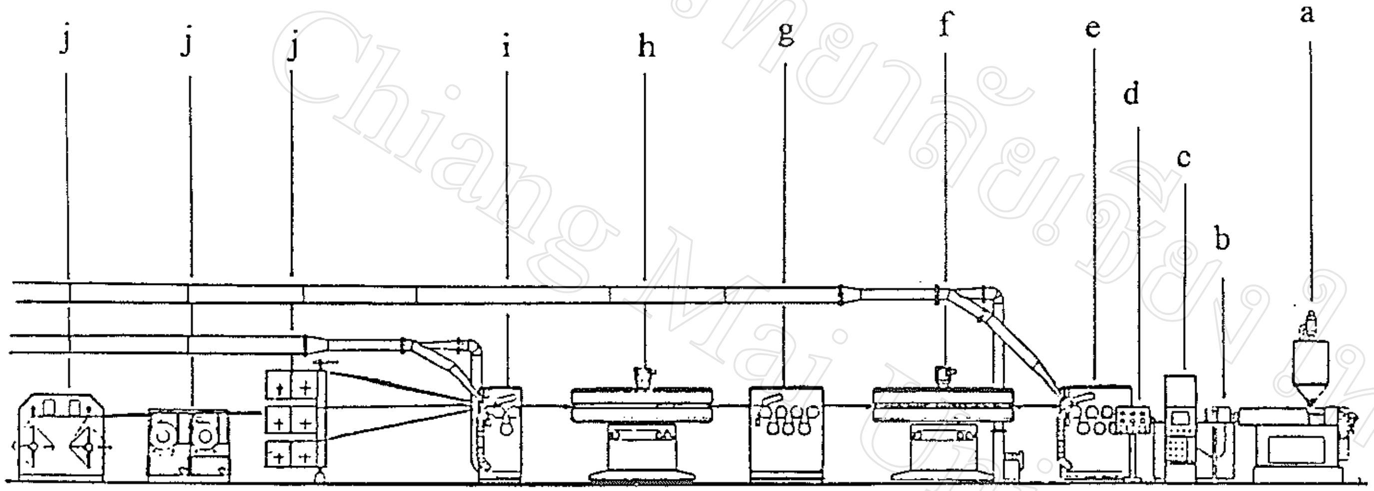


Fig. 2.1 Polypropylene monofilament production line with single-step drawing; drawing in hot-air oven [16].
(a) extruder, (b) monofilament die, (c) processing control system,
(d) control panel, (e) draw unit I, (f) hot-air oven I, (g) draw unit II
(h) hot-air oven II, (i) draw unit III, (j) wind-up units.

2.2.3 Drawing

Polypropylene fibres are usually drawn to increase orientation and modify the physical properties of the fibre further. Linear density, necessary to control the textile properties, is more easily reduced during drawing than in spinning. The draw step can be accomplished in line with spinning in a continuous spin-draw-texturing process but is more commonly done in a second process step. To relieve internal strains, the filaments are heat-set or annealed. This last step also aids in the development of a more perfect crystal structure. Fibres with a degree of crystallinity of about 70% can be obtained under optimum quenching and annealing conditions. Orientation has been found to be the most important structural variable as far as mechanical properties are concerned. Orientation can be achieved by drawing or high-speed spinning.

2.2.4 Properties

Mechanical and Physical. Typical mechanical and physical properties of polypropylene fibres are given in Table 2.1. Of particular interest are the low density, allowing much lighter-weight fibre at a specified size or coverage, and the low moisture absorption. The moderate melting temperature of polypropylene is high enough for most applications, but low enough to permit thermal bonding more easily than in most other fibres.

Chemical. The hydrocarbon nature of olefin fibres, lacking any polarity, imparts high hydrophobicity and, consequently, resistance to soiling or staining by polar materials. At room temperature, polypropylene is resistant to most organic solvents, except for some swelling in chlorinated hydrocarbon solvents. At higher temperatures, polypropylene dissolves in aromatic or chlorinated aromatic solvents, shows some solubility in high boiling hydrocarbon solvents, and can be degraded by strong oxidizing acids.

Table 2.1 Typical mechanical and physical properties of polypropylene fibres [13,15].

Properties	Values
Tenacity at break, N/tex[a]	
65% r.h., 21°C	0.44 - 0.79
wet	0.44 - 0.79
Tensile strength, kgf/mm^2	
continuous filament yarn	60
monofilament	35
Extension at break, %	
65% r.h., 21°C	15 - 30
wet	15 - 30
Young's modulus, kgf/mm^2	
continuous filament yarn	650
monofilament	325
Specific gravity	0.90 - 0.92
Volumetric swell in water	none
Melting range, °C	165 - 175
Refractive index (η)[b,c]	
$\eta_{\parallel}$	1.530
$\eta_{\perp}$	1.496
Birefringence ($\eta_{\parallel} - \eta_{\perp}$)	0.034

[a] To convert N/tex to g-f/den, multiply by 11.3

[b] $\eta_{\parallel}$ = refractive index parallel to the fibre axis

[c] $\eta_{\perp}$ = refractive index perpendicular to the fibre axis

Thermooxidative stability. The thermooxidative stability of polypropylene fibre is poor. It is highly sensitive to oxygen which must be carefully controlled in all processing operations, particularly fibre processing. In particular, it is the tertiary hydrogen atoms in polypropylene which impart sensitivity to oxidative degradation. Consequently, polypropylene fibre is usually stabilized by hindered phenols or substituted amines during processing.