CHAPTER 1

INTRODUCTION

World demand for synthetic-polymer fibres has grown steadily at a rate of 20-25 % per annum for the last quarter-century (1). Polyester, polyamide (nylon), and acrylic fibres are now three principle man-made fibres. Apart from these three types, olefin fibres (especially polypropylene fibres) seem to be the most important of all other synthetic fibres and to be the one most likely to challenge the three leading synthetic fibres in the longer term.

Olefin fibres (2,3,4), which also are called polyolefin fibres, are manufactured fibres in which the fibre-forming substance is any long-chain synthetic polymer of at least 85 % by weight, of ethylene, propylene, or other olefin units, except amorphous (noncrystalline) polyolefins qualifying under category [1] of paragraph [j] of Rule 7-Generic Names and Definitions for Manufactured Fibres (Federal Trade Commission, Textile Product Act). The olefin fibres of commercial importance are polypropylene (PP) and, to a lesser extent, polyethylene (PE). But there are still some fibres produced on a laboratory scale from several other polyolefins, e.g. poly(1-butene), and poly(3-methyl-1-butene), etc.

Polyropylene textiles are produced in substantial quantities throughout the world, rivalling wool in total tonnage. Polypropylene is not new, its invention dating from 1954 and commercialization from about 1960, but it was the last major fibre material to be introduced. Although several other important fibres have appeared more recently, all are of smaller production and specialized in properties. The position of polypropylene relative to the other man-made fibres is shown in the world production statistics given in Table 1.1 below (5).

Table 1.1 World production of principle man-made fibres in 1985 (1000 tonne units)

FIBRES	PRODUCTION
Cellulosic(viscose,acetate)	3,264
Polyamide	3,398
Polyester	6,558
Acrylic	2,411
Polypropylene(inc. film-type)	1,500

1.1 METHOD OF MANUFACTURE (6-9)

Polypropylene was invented in its present form in Italy in 1954 by Professor Giulio Natta and Professor Ziegler. Both Professors had demonstrated new catalyst system, namely Ziegler-Natta catalysts (7,8,9) that

enabled conversion of the gas propylene into the hard plastic, polypropylene. These catalysts are based on some form of titanium (III) chloride ($TiCl_3$) and an aluminium alkyl or alkyl halide. Mixed metal-alkyls such as lithium aluminium alkyls and various metal hydrides are also commercially used.

Propylene ($CH_3CH=CH_2$), the monomer of polypropylene manufacturing, is one of the gases liberated during crude oil refining and it is also available as a fraction of natural gas (5-8).

In one of the recent polypropylene manufacturing processes, there are five key steps involved (Figure 1.1), namely,

1. Catalyst preparation.
2. Polymerization.
3. Purification.
4. Recovery of solvents.
5. Compounding and finishing.

The simply description of process illustrated in Figure 1.1 is to polymerize propylene gas with the aid of Ziegler-Natta Catalysts in a diluent. The polymer formed from the propylene is slurried in the diluent to decompose the catalyst, and is then filtered, purified, and reduced to powder form as polypropylene resin. Additives may be included in the resin to stabilize the relatively low inherent heat and light degradation properties of polypropylene.
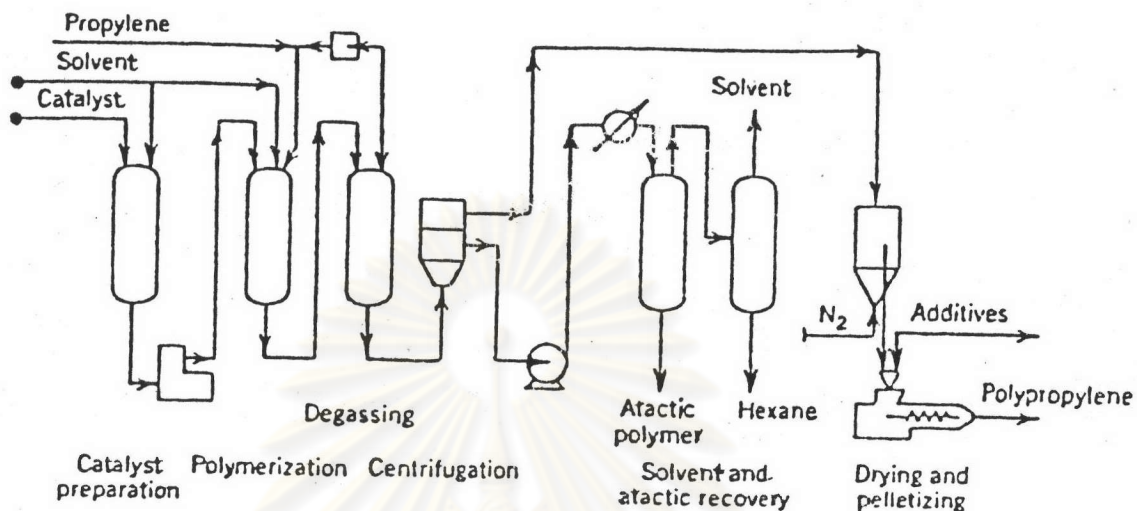
Figure 1.1 High yield Montedison polypropylene process (8)

The resin is melted and extruded through a spinneret in
filament form (5,10) (Figure 1.2). The filaments are then
treated and drawn to get the proper crystallinity and
molecular orientation in order to obtain such desired
characteristics as strength, abrasion resistance, elasticity,
resilience, and shrinkage. The fibre may be heat-set to
alter its shrinkage, elasticity, and flex-resistance
characteristics.

Polypropylene may also be extruded in sheet form
and subsequently fibrillated or slit, to form tape yarns
(5,11). The process and some descriptions of tape yarn
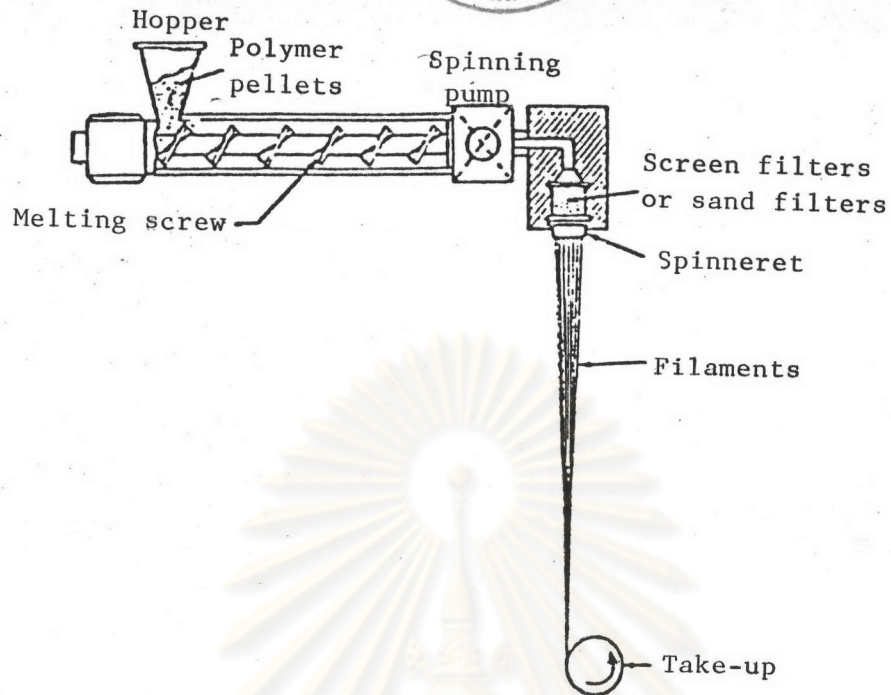will be mentioned in later section.

Figure 1.2   Schematic Melt-Spinning Process (2)

1.2   THE PURPOSES OF THIS STUDY

In this study, polypropylene tape yarn was preliminarily dyed with various disperse dyes of both azo and anthraquinone structure. Subsequently, the studies involving various aspects were:

1.   The determination of the most suitable dye, of all dyes used, for the subsequent studies.

2.   The effect of temperature on dyeing.

3.   The effect of carrier concentration on dyeing.

4.   The light fastness of dyed tape yarn.

1.3 HISTORICAL

The interest in this polymer, polypropylene, essentially derives from its good mechanical properties and from the attraction of being produced from a cheap monomer. Unfortunately, polypropylene fibres are difficult to dye since they (in isotactic structure) are very highly crystalline, very hydrophobic and hence do not swell in aqueous systems; nor do they contain any polar groups or aromatic ring systems. Indeed, because of the aliphatic nature of the polymer, interaction between dyes and the polymer chains may be expected to be weak.

When polypropylene was first produced, most of the dye ranges were tried and rejected because they were only sorbed to small extents. Only disperse dyes (and chemically related compounds) showed any promise. As might be expected, those dyes which are hydrophobic are sorbed: the degree of sorption improves with increase in the hydrophobic character of the dye.

The dyeing of polypropylene fibres can be generally classified into 2 categories (1,12), according to the features of fibres to be dyed, as in the following:
1. Dyeing of modified polypropylene
2. Dyeing of unmodified polypropylene

1.3.1 Dyeing of Modified Polypropylene (1,12-14)

Many techniques are developed before the

dyeing are carried out. Depending upon the technique applied, polypropylene fibre acquires affinity for various dyes like disperse dyes, acid dyes, basic dyes, and mordant dyes, etc. The techniques include

(i)   Copolymerization with other inert monomers.

(ii)   Grafting of other polymers onto an isotactic polypropylene.

(iii) Blending with other inert polymers before extrusion.

(iv)   Dissolving or dispersing inert additives of low molecular weight in the polymer melt.

(v)   To prepare the dyes specifically for the purpose.

(vi)   Partial oxidative degradation of polypropylene.

1.3.2 Dyeing of Unmodified Polypropylene(1,12,13,15)

Unlike the description in section 1.3.1 above, polypropylene in its original feature can be dyed with selected dyes without any modification of the polymer or mixing some dye-receptive additives. Comparing with the above kind of dyeing, dyeing in this way can be achieved with low cost, less time, less stages to be processed, etc., but unsatisfied results involving some poor exhaustion, some poor fastness, i.e. to washing and dry cleanings than the above one are obtained. The dyes for dyeing generally are disperse dyes, vat dyes applied and azoic combination, etc., with the former one is of more importance for the coloration of unmodified polypropylene.

Teramura et al (16,17) had shown that azo and anthraquinonoid disperse dyes containing hydrophilic hydroxyalkyl groups had no substantivity for polypropylene and that, in general, substantivity increased with the hydrophobic character of the dye.

Vercinigte Glanzstoff-Fabriken, ACNA and ICI claimed that incorporation in the molecule of a long alkyl chain gives disperse dyes exhibiting good fastness on polypropylene fibre.

Katajama et al (18) had examined the equilibrium behaviour of Dimethyl Yellow (C.I. 11020) and three hydrophilic disperse dyes (C.I. 11210, its 2,5-dichloro derivative and C.I. 11100) at different temperatures in the presence of polypropylene fibre. In each case a linear adsorption isotherm was obtained, leading to values for affinity, heat of dyeing and entropy change.

Bird and Patel (15) had examined the behaviour on unmodified polypropylene fibre and film of two commercial disperse dyes and Dimethyl Yellow. The results indicated that disperse dyes capable dyeing polypropylene fibre had high diffusion coefficients and low saturation values. Linear adsorption isotherms were obtained with Dimethyl Yellow.

Mangan (19) had suggested a prototype for a new class of dyes adapted especially for polyolefins. Two distinctly different polypropylene fabric types were used

for the dyeings. Preliminary dyeings were done with the disperse dye to explore dye/substrate interaction. Sorption isotherm studies revealed a Nernst isotherm. Dye yield on the fibre was as high as 90 % and deep shades were obtained.

1.4 POLYPROPYLENE TAPE YARN (3,5,11)

More than half of all polypropylene textiles are based not on extruded fibres but on tape (or strip, or film tape) yarns slit from wider extruded film, or sometimes extruded as tapes from elongated slot dies. These tapes are variously twisted to form string, twine, and rope, or used flat for weaving.

There is some uncertainty as to whether these tape yarns can be classed as textile fibres or not. In the United Kingdom, the Statutory Instrument of Government on Trade Descriptions (1986, no. 26) includes under "textile fibre" - "flexible tubes or strips, including strips cut from wider strips or films which (i) have an apparent width which does not exceed 5 mm, and (ii) are produced from (listed) substances used in the manufacture of fibres".

Most weaving tapes of polypropylene are 2-3 mm in width, and they have textile-like, flexible, fibrous properties, therefore, they are acceptable as "fibre".

1.4.1 Production of Tape Yarn (5,11)

Polypropylene polymer pellets are melted and extruded through a flat die to give a film, which is water-quenched or brought into contact with cooled rollers ("chill rolls") to solidify the film. Alternatively the film may be produced by extrusion through a circular die vertically upwards, the balloon so formed being collapsed and brought back down to a horizontal position as a double layer of film ("blown film"). Following extrusion, the film is slit into tapes which are hot-stretched with a draw ratio of about 8:1 or more and wound up on bobbins, for use as weaving yarns in widths often of 2-3 mm.

1.4.2 Uses of Tape Yarn (5,11)

The main uses are in woven fabric, using modern shuttleless looms that lay the tapes as weft in untwisted condition, giving very high covering power. The principle uses are primary backing for tufted carpets, sacks, and bale wrap, flexible intermediate bulk containers (FIBCs), construction industry protection fabric, and some smaller uses including secondary carpet backing, furniture under-fabrics, and webbing. Polypropylene tape yarns are also twisted to form harvest twine, displacing sisal twine. Ropes formed from polypropylene tape strands occupy a cheaper, less-extensible role and are widely used in industry, agriculture, marine gear, and fishing. Twisted twines and cordage are made into nets for fishing, industry, and games.
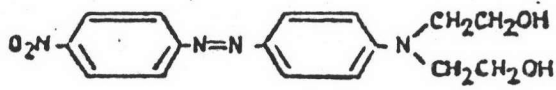
1.5 DISPERSE DYES (20,21)

This class of dyes were variously known as acetate dyes, dispersed acetate dyes, dispersion dyes and dispersol dyes. But the present universally accepted name, "disperse dyes", was introduced in 1951 and first defined in 1953. It is currently defined as "substantially water-insoluble dyes having substantivity for one or more hydrophobic fibres, and usually applied from fine aqueous dispersion".

Fine uniform dispersion is necessary to distribute the dye evenly throughout the dyebath, prevent filtration of the dye by the fibres being dyed and more specifically to present a large surface area of dye particles from which rapid dissolution may take place to replace that taken up by the fibre during dyeing.

Disperse dyes are essentially low molecular weight derivatives of azo, anthraquinone, diphenylamine and other compounds. They melt at above 150 °C and are crystalline materials, which are ground with dispersing agents to produce particles of 0.5-2 μ in size, and which produce a stable dispersion in the dyebath. They are essentially nonionic in nature though they contain aromatic or aliphatic amino, mono- and disubstituted amino and hydroxy groups in their molecular structure. They have relatively low solubility in water under the dyeing conditions. They do not undergo any chemical change during dyeing.
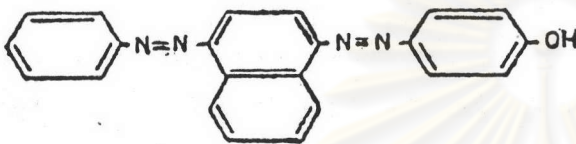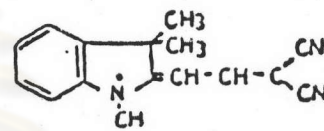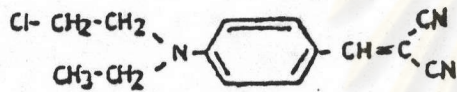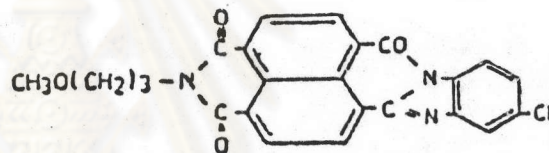
Monoazo Dye
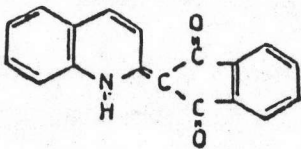
Anthraquinonid Dye
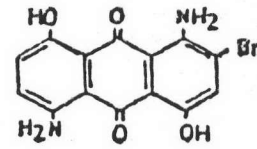
Disazo Dye

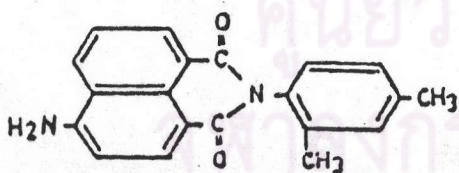Methine Dye

Styryl Dye

Acroylene Benzimidazole Dye

Quinonapthalone Dye

Nitro Dye

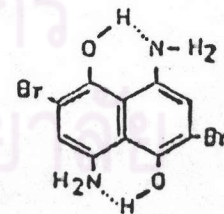Aminonaphthylamide Dye

Naphthoquinoneimine Dye

Figure 1.3   Chemical structures of disperse dyes (20)

The chemical structure of disperse dyes are, namely, about 50 % of all the commercial disperse dyes belong to monoazo dyes and 25 % is provided by anthraquinonoid dyes. Diazo contributes 10 % of the total, while the remainder of the total belong to methine, styryl, acrylenebenzimidazol, quinonaphthalone, aminonaphthylamide, naphthoquinone-imine and nitro disperse dyes. Some typical structures of these dyes are given in Figure 1.3.

1.6 CARRIER (6,20,22,23)

Some fibres which are more difficult to dye because of their low rates of dye sorption at low temperature, adequate rates are only achieved when the dyeing are carried out at high temperature. In practical conditions, economic speeds of dyeing are achieved by dyeing at high temperatures, i.e. at or above the boil. An alternative method of speeding up the rate is to add certain low molecular weight compounds; these substances are rapidly adsorbed and markedly accelerate the rate of dyeing. Dyeing can then be achieved in an economic time at normal dyeing temperatures. Such compounds are referred to as "accelerators or carriers". The word "carrier" was coined because it was originally suggested that it "carried" the dye molecules into the fibre.

Carriers are not needed for the dyeing of natural fibres because natural fibres have an open, partially hollow structure and are easily penetrated by dye solutions in water.

Carriers have been recommended for dyeing many synthetic fibres, such as cellulose triacetates, polyacrylics, polyamides and polyesters which are somewhat hydrophobic but have found their greatest use in the dyeing of the latter one. And for this study, a carrier of methyl naphthalene type is subjected into consideration for its influence on dyeing polypropylene, which is also hydrophobic and somewhat more hydrophobic than any other fibres by considering their relative rates of water imbibition (Table 1.2) compared to viscose.

Table 1.2 Rate of water imbibition of fibres compared to viscose (23)

FIBRE	WATER IMBIBITION (%)
VISCOSE	100
ACETATE	25
TRIACETATE	10
POLYAMIDE	11-13
POLYACRYLIC	8-10
POLYESTER	3
POLYPROPYLENE	0

While selecting a carrier for use in dyeing, the following points may be considered (20): high efficiency; availability at low cost; little or not effect on the fastness of the final dyeing; absence of unpleasant odour;

non-toxicity; no degradation or discolouration of the fibre; easily removable after dyeing; high stability under dyeing conditions; compatibility with the dyestuff; sparingly water soluble, but easy to emulsify or to disperse; low volatility and uniform absorption by the fibre.

Most carriers are aromatic compounds and some of the compounds most commonly used as dye carriers are show in Table 1.3 (23).

Table 1.3 Compounds most commonly used as dye carriers (23)

	mol. wt.	bp, °C
Phenolic compounds		
o-phenylphenol	170.2	280-284
p-phenylphenol	170.2	305-308
methyl cresotinate	166.0	240
Chlorinated aromatic compounds		
o-dichlorobenzene	147.0	172-178
1,3,5-trichlorobenzene	181.45	214-219
Aromatic hydrocarbons and ethers		
biphenyl	154.2	255.9
methylbiphenyl	168.24	255.3
diphenyl oxide	170.0	259.0
1-methylnaphthalene	142.2	244.6
2-methylnaphthalene	142.2	241
Aromatic esters		
methyl benzoate	136.14	198-200
butyl benzoate	178.22	250
benzyl benzoate	212.24	323-324
Phthalates		
dimethyl phthalate	194.18	298
diethyl phthalate	212.18	298
diallyl phthalate	246.25	290
dimethyl terephthalate	194.18	284