

Part I

Polyester and polyamide fundamentals

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1.1 Introduction

Among the polycondensation polymers, the most important and widely used today is polyesters; and equally important is polyamides. Polyesters can be processed by melt spinning, injection and/or blow moulding and film extrusion whereas polyamides can be processed by melt spinning and injection moulding and extrusion. More details on polyamides are given in [Chapter 2](#). Polyesters are widely used as packaging materials such as bottles/containers, film, and so on, and also as a fibre, filament, fabrics in textiles and as a base material for photographic film and recording tape applications. The term ‘polyester’ is used for polymeric materials containing ester groups in the polymeric main chains of macromolecules and not to the ester groups in the side chains of the macromolecules, as in the case of poly(vinyl acetate) (or) poly(methyl methacrylate), etc. The term ‘polyester’ is applicable to products derived from dicarboxylic acids and diols. However, the term is not restricted to derivatives of dicarboxylic acids but also to other types of acids such as phosphonic (or) sulphonic (or) phosphoric acids. This chapter is restricted to polyesters derived from dicarboxylic acids and diols alone. Chemical structures of various dicarboxylic acids and diols that are used to make polyesters or copolyesters are given in [Table 1.1](#). Even though large number of polyesters and copolyesters can be prepared by varying dicarboxylic acids and diols and by varying the content of comonomers, only some of them are commercialised and trade names of these polyesters are listed in [Table 1.2](#). Some of the major polyester manufacturers and their capacity are listed in [Table 1.3](#). Even though polyesters have many useful properties, they are blended or alloyed with other polymers to overcome some of the polyester shortcomings. [Table 1.4](#) shows the list of trade names of some of the commercialised polyester blends or alloys.

Table 1.1 Chemical structure of various dicarboxylic acids/diols

Dicarboxylic acid/Diol	Structure
Terephthalic acid	<p style="text-align: center;">PTA</p>
Isophthalic acid	<p style="text-align: center;">IPA</p>
2,6-Naphthalene dicarboxylic acid	<p style="text-align: center;">NDA</p>
Lactic acid	<p style="text-align: center;">LA</p>
Monoethylene glycol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ <p style="text-align: center;">MEG</p>
1,3-Propane diol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ <p style="text-align: center;">PDO</p>
1,4-Butane diol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ <p style="text-align: center;">BDO</p>
1,4-Cyclohexane dimethanol	<p style="text-align: center;">CHDM</p>

1.2 Classification

Polyesters are broadly classified into two types, namely: (i) thermoplastic polyesters and (ii) unsaturated polyesters, which upon curing form highly cross-linked thermosets. Thermoplastic polyesters can be further classified into six types: (i) Linear aromatic polyesters, which are mouldable, film-forming and fibre-forming polyesters; (ii) Elastomers, which are block

Table 1.2 List of trade names of polyesters

Polyester	Trade name	Company	Form
PET	Amilar		
	Blue C	Monsanto Co.	Fibre
PET	Dacron	DuPont	Fibre
PET	Daiya foil		
PET	Diolen	Glanzstoff AG	Fibre
PET	Dowlex		
	Encron	American Enka Corp	Fibre
PET	Fiber V		Fibre
	Fortrel	Fiber Industries Inc	Fibre
PET	Grisuten	VEB Chemiefaserwerk	Fibre
PET	Hostadur		
PET	Hostphan	Hoechst	Film
	Kodel	Eastman Chemical Products, Inc	Fibre
PET	Kuraray	Kurashiki Rayon KK	Fibre
PET	Lavsan		
PET	Lawsonite		
PET	Melinex	ICI	Film
PET	Mersilene		
PET	Nitiray	Nippon Ester Co. Ltd	Fibre
PET	Nitron lavsan		
PET	Eastapak	Eastman	
PET	Melinar	ICI	
PET	Impet	Ticona (Hoechst)	Engg. Glass filled
	Toyobo	Toyobo Co. Ltd	Fibre
PET	Caripak	Shell	
	Lavsan	USSR Government	Fibre
PET	Mylar	DuPont	Film
	Okson	USSR Government	Fibre
	Quintess	Phillips Fibers Corp	Fibre
PET	Teijin-Tetoron	Teijin Ltd	Fibre
PET	Terylene	ICI Fibres Ltd	Fibre
PET	Tergal	Société Rhodiaceta	Fibre
PET	Terital	Société Rhodiatocé	Fibre
	Toray-Tetoron	Toyo Rayon KK	Fibre
	Tersuisse	Société de la Viscose Suisse	Fibre
PET	Tralbe	Société Rhodiaceta	Fibre
PET	Terylene	Millhaven Fibers Ltd	Fibre
PET	Trevira	Austria Faser GmbH	Fibre
PET	Trevira	Farbwerke Hoechst	Fibre
	Trevira	Hystron Fibers, Inc	Fibre
PET	Vestan	Faserwerke Huls GmbH	Fibre
	Vycron	Beaunit Fibres Division	Fibre
PET	Wistel	Snia Viscosa	Fibre
PET	Rynite	DuPont	Engg.
PET	Ashlene	Ashley	
PET	Petra	Honeywell	Engg.
PET	Eco Vylopet	Toyoda Gosei Co.	Engg.

Table 1.2 cont'd

Polyester	Trade name	Company	Form
PTT	Corterra	Shell	Fibre
PTT	Sorona	DuPont	Fibre
PBT	Valox	GE	
PBT	Crastin	DuPont	
PBT	Arnite	DSM	
PBT	Ultradur	BASF	
PBT	Celanex	Polyplastics Ticona	
PBT	Tribit	SamYang Kasei	
PBT	LuPox	LG Chemicals	
PBT	Lutrel	LG Chemicals	
PBT	Pocan	Bayer	
PBT	Durlex	ChemPolymer	
PBT	Hiloy	ComAlloy	
PBT	Voloy	ComAlloy	
PBT	Vexel	Custom Resins	
PBT	Spesin	Kolon	
PBT	Grilpet	EMS-American Grilon	
PBT	Ashlene	Ashley	
PCT	Thermx	Eastman	
PCT	Kodel	Eastman Kodak Co.	
PCT	Vestan	Chemische Werke Huls	

Table 1.3 List of polyester manufacturers and capacity

PET suppliers	Capacity (KMTA)
Futura Polyesters Ltd	118
Reliance Industries Ltd	2500
Indorama	600
South Asia Petrochemicals	140
JBF	414
Eastman Chemicals	1473
KoSA	865
Wellman	390
M & G	580
Nanya	200
DuPont	415
Rhodiaster	177
Dow	280
Kohap	206
Shin-Kong	160
Tong-Kook	140
Far Eastern	120

Table 1.4 List of trade names of polyester blends/alloys

Blend/alloy	Trade name	Company
PET/PBT	Valox 800 series	GE Plastics
	Celanex 5000 series	Hoechst-Celanese
PET/PC	Makroblend	Mobay / Bayer
PBT/PC	Xenoy	GE Co.
	Makroblend PR	Mobay
PC/PET (or) PBT	Koblend	Enichem
	Sabre 1600	Dow Chemicals
	Stapron E	DSM
Polyester/PC	Edgetek	Polyone
	Comtuf	ComAlloy
	Ultradur	BASF
	Eastalloy	Eastman
	Valox	GE Plastics
PBT/ABS	Naxaloy	MRC Polymers
	Cytra	GE Co.
	Dialoy B	Mitsubishi Rayon
PET/Par*	Macalloy B	Japan Synthetic Rubber
	Ardel D-240	Amoco
	U-8000	Unitka
PBT	Enuran	GE
PET/polysulfone	Mindel B	Amoco
PBT/acetal	Duraloy	Hoechst-Celanese
PET/PTFE	RTP 1100	RTP Co.
PBT /PTFE	RTP 1000	RTP Co.
PET/PEI	Ultem 1285	GE Co.
Polyester/TPU	Texin	Bayer
	Desmopan	Bayer
	Pellethane	Dow
Polyester/TPE	Hytrell	DuPont
	Ecdel	Eastman
	Kopel	Kolon
	Arnitel	DSM
	Lomed	GE
	Retiflex	Hoechst-Celanese
	Pelprene	Toyobo
	Elitel	Elana

Notes:

* Bisphenol A polyarylates

TPU – Thermoplastic Urethane

TPE – Thermoplastic Elastomer

copolyesters containing stiff and flexible parts; (iii) Liquid crystalline polyesters (LCP), which are typified by very high strain modulus and strength and low strains to break; (iv) Engineering plastics, which are strong, stiff, tough and highly crystalline; (v) Aliphatic polyesters such as polycaprolactone, polylactides, polyglycolides, which are obtained by

ring-opening polymerization of cyclic monomers or dimers; and (vi) Poly(hydroxyl alkanooates) such as poly(3-hydroxy butyrate) [P(3HB)], poly(3-hydroxy valerate), which are found to be biodegradable and biocompatible and are produced from selected carbon substrates such as glucose, gluconates or methanol by a variety of micro-organisms via a fermentation process. Monsanto's Biopol® is commercially available PHA based polyester.

Linear aromatic commercial polyesters are classified into two types based on the type of aromatic moiety present in the polyester main chain. They are (i) phthalates and (ii) naphthalates. Polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), polybutylene terephthalate (PBT) belong to the phthalate group because these polyesters were derived from purified terephthalic acid (PTA) (or) dimethyl terephthalate (DMT). Polyethylene isophthalate (PEI) also belongs to phthalate group and was derived from isophthalic acid (IPA) (or) dimethyl isophthalate (DMI). PEI has a glass transition temperature of 51°C. Some of the PTA and DMT manufacturers are Sabic, Mitsubishi, Indian oil, etc. Similarly, Polyethylene naphthalate (PEN), polytrimethylene naphthalate (PTN) and polybutylene naphthalate (PBN) belong to the naphthalate group as these were derived from 2,6-naphthalene dicarboxylic acid (NDA) (or) dimethyl-2,6-naphthalene dicarboxylate (NDC). Both NDA and NDC are commercially produced by BP (British Petroleum). NDC is being manufactured by Mitsubishi Gas Chemical Co. and Amoco. NDA is being manufactured by Frinton Laboratories, Inc. and Kinbester Co. Ltd. When compared to NDC, the availability of NDA is very much limited. The purity of commercial NDA is usually below 95 per cent and the high purity grade (98 per cent) is obtained from alkaline hydrolysis of NDC followed by acidification, which renders this process commercially not viable. NDA and NDC are more expensive than PTA or DMT. Naphthalate moieties in the polymer chain were found to: increase glass transition temperature; increase continuous use temperature; increase heat deflection temperature; increase barrier to oxygen, carbon dioxide, water vapour and gasoline; increase UV absorption cut-off; and increase stiffness and strength but naphthalates are more expensive than terephthalates due to increased cost of NDC/NDA.

1.3 History

Since ancient times, natural polyesters have been known to mankind. Shellac, natural polyester, as secreted by the lac insect, was used by the ancient Egyptians for embalming mummies. Berzelius first synthesized polyesters of polybasic acids and polyvalent alcohols (Berzelius, 1847) by reacting tartaric acid and glycerol.

Polyesters were initially developed for coating applications and are commonly known as 'alkyd resins'. The term 'alkyd' was coined by combining the first part of the word 'alcohol' and the last part of the word 'acid'. Alkyd resin was first marketed by the General Electric Co. of the USA, with the trade name of Glyptal®, which has become an alternative name to alkyd resin (Kienle and Hovey, 1929). Glyptals were produced by extended condensation reactions involving glycerol, phthalic anhydride and the fatty acids of various oils such as linseed oil, soyabean oil, dehydrated castor oil and tung oil. The unsaturation present in the fatty acids of the oils undergoes aerial oxidation on ageing and become progressively less soluble or insoluble. The oxidation reaction was catalysed by cobalt or manganese naphthenates, which are commonly known as driers. Other polyhydric alcohols such as MEG, propylene glycol/1,3-propane diol (PDO), pentaerythritol and sorbitol and acids namely maleic anhydride, IPA, terephthalic acid and could be used to vary the useful properties of alkyd resins.

Unsaturated polyesters were later developed as laminating resins of fibre reinforced composites. These resins were made by polycondensation reactions involving varied proportions of saturated acids such as phthalic anhydride, IPA, adipic acid and unsaturated acid namely maleic anhydride and a glycol such as MEG, PDO, DEG, etc. These resins could be cured at room temperature using methyl ethyl ketone peroxide and cobalt (or) copper naphthenate (or) octoate. Alternatively, benzoyl peroxide, N, N-dimethyl aniline could be used.

In the late 1920s, W. H. Carothers made a large number of polyesters ranging in molecular weight between 2500 and 5000 by condensation reactions of dicarboxylic acids and diols. In 1930s, Carothers and Arvin (1929) synthesized polyesters having a molecular weight of ~4000 by reacting octadecanedioic acid with PDO (dicarboxylic acids with 5 per cent excess of diols). Carothers and Hill increased the molecular weight to 12000 (Carothers and Hill, 1932). This polymer was known as 3-16 ester based on the number of methylene groups in diol and dicarboxylic acid respectively. Later this polymer was known as 3G18 based on the number of carbon atoms in diol and dicarboxylic acid including the carbonyl carbon atom. Carothers and J. W. Hill obtained higher molecular weight polyester up to 25000 by removing the water liberated in the condensation reactions of the step-wise polymerization. Carothers coined the term 'Super Polymers' for the polyesters having molecular weights above 10000 because the properties of these polymers were so different from the polymers having low molecular weight i.e., <10000. Super Polyesters were tough, opaque solids which melted to clear viscous liquids at elevated temperatures. Filaments could be drawn by pulling the molten polymer using a glass rod. After allowing the filaments to cool, these filaments could be drawn to

several times their original length. These filaments became transparent, tough and possessed high tenacity.

1.4 Polymerization methods

With respect to the equipment and the conditions followed, the polymerization step in polyesters is similar to that of polyamides. On comparison, the formation of high molecular weight in polyesters differs to some extent. The chemical equilibrium favours the polyamide formation, whereas the equilibrium is much less favoured in polyester; stoichiometric equivalence is easily achieved by the use of salts in polyamides whereas due to the non-formation of salts, the stoichiometric equivalence is more difficult to achieve in polyesters; and the amide interchange reactions are slow, when compared to polyesters.

1.4.1 Step-growth polycondensation

Polyester is formed by step-growth polycondensation from dicarboxylic acid or its diester and diol. The by-products produced are water (or) methanol depending upon the reactant used namely dicarboxylic acid or its dimethyl ester. A number of catalysts are used for the polycondensation reactions such as compounds on antimony, germanium, titanium, aluminium, etc. Antimony based catalysts are used at a dosage level of 300 ppm whereas titanium based catalysts are used at about 20 ppm dosage level. As a result polyesters prepared from titanium based catalysts contain lesser amounts of residual catalyst. Germanium catalyst is expensive and widely preferred in Japan. Enzyme protease from *Bacillus licheniformis* can also be used as a catalyst for the transesterification of DMT and diol in the synthesis of aromatic polyesters in anhydrous tetrahydrofuran (THF).

1.4.2 Ring-opening polymerization

Polyesters can be prepared by ring-opening polymerization (ROP) (Jerome and Teyssie, 1989; Penczek and Slomkowski, 1989) using cyclic oligomers and polymerization could be achieved at temperatures well below the melting point of the final polymer. Unlike polycondensation reaction, this method does not require removal of any by-products and high molecular weight of >100000 can be achieved in a matter of minutes. Using this method, PET and PBT can be prepared using the corresponding cyclic oligomers. The limitations of this technique are that one has to synthesize cyclic oligomer using diol and diacid chloride and that a solvent and catalyst are required.

1.4.3 Polyaddition reaction

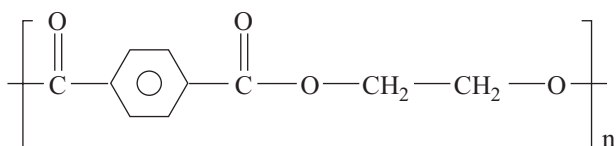
Alternatively, polyesters can be prepared by polyaddition reaction of diepoxides to diacids (Madec and Marechal, 1985). This reaction is catalysed by amines, quaternary ammonium, antimony trioxide, antimony pentachloride, Ph_3As . A comprehensive review is reported elsewhere (Madec and Marechal, 1985). Polyaddition reaction is accompanied by the numerous side reactions, which limits its use, where linear polyesters are required. The important side reactions are opening of epoxy ring by water to give hydroxyl pendant groups, which in turn can react with carboxyl end group (or) epoxy ring. These polyesters are used as composites, blends, laminates and biodegradable polymers.

1.4.4 Recycling

Polyesters can be recycled either by physical (or) chemical methods. In the physical recycling method, post-consumer recycled PET flakes are remelted in an extruder for pelletization into chips or direct melt processing into value-added products. Chemical recycling is versatile because it is capable of removing any additive contamination and any type of PET waste can be used. In chemical recycling method, hydrolysis (Pitat, 1959) or methanolysis (Anon, 1959) or glycolysis (MacDowell, 1965) is used. Hydrolysis is carried out under high pressure water or steam or aqueous sodium hydroxide solution at 180–250°C under pressures of 1.4–2 MPa or strong inorganic acid such as nitric acid, sulphuric acid at 85–150°C. Methanolysis involves depolymerization of PET waste in a large quantity of methanol in the presence of catalyst at high pressure and temperature for 3–5 hours (Vaidya, 1988). The depolymerization of PET in the presence of significant excess of glycols such as MEG at elevated temperatures (180–250°C) is termed glycolysis. Post-consumer recycled PET flakes are depolymerised into either the monomers namely PTA or DEG, MEG or into oligomers. Then these monomers or oligomers are reconverted into PET by polycondensation reaction or to unsaturated polyesters by polyaddition reaction. Recycled PET is used for making coarse denier staple fibres (>3 dpf) for carpets, needle-punched non-wovens, tennis ball covers, etc. and for making hollow fibres or as geotextiles for soil stabilisation, silt fencing, rail-bed stabilisation, etc., hollow fibres for filling, partially oriented yarns, dope dyed fibres or filament yarns and strappings for packaging. The use of recycled PET in producing film and sheet products is limited to those applications where clarity, transparency and colour are not of prime importance.

1.5 Poly(ethylene terephthalate) (PET)

The most commercially important aromatic polyester is poly (ethylene terephthalate) (PET). Among the aromatic polyesters, PET is considered as 'work horse'. PET is otherwise known as polyethylene glycol terephthalate, ethylene terephthalate polymer, poly (oxy-1, 2-ethanedioylcarbonyl-1, 4-phenylene dicarbonyl), terephthalic acid-ethylene glycol polyester. It is also known as 2GT. PET is a white or light cream material, has high heat resistance and chemical stability and is resistant to acids, bases, some solvents, oils and fats. The unit molecular weight of PET is 192 and the chemical structure of PET is given below:



The refractive index of PET is 1.574 @ 25°C. PET is insoluble in water and due to hygroscopic nature; it picks up moisture very fast and needs sufficient drying to minimise the drop in intrinsic viscosity (IV) during processing. The abrasion resistance of PET is 60 mg/1000 cycles. PET stands first among all the man-made fibres and challenges cotton with a steady growth rate of about 5 per cent. PET has higher UV absorption cut-off (313 nm) than polycarbonate (290 nm), poly(methyl methacrylate) (285 nm) and high density polyethylene (225 nm). Neither administration of PET powder nor a single administration of chloroform extracts of PET at a dose of 10 g/kg BW had a toxic effect on rats. USFDA approved the use of PET as components of polyethylene phthalate polymers intended for use in contact with food in accordance with the conditions prescribed in 21 CFR part 177.1630. PET fibres display good resistance towards sunlight and are surpassed only by the acrylics. The resistance to mildew, ageing and abrasion is generally considered excellent.

1.5.1 Polymer production

Like any other polyester, there are many routes to produce PET. The most commonly practised ones are: (i) the dimethyl terephthalate (DMT) route and (ii) the purified terephthalic acid (PTA) route. Raw material purity plays an important part with polymer purity. The inhomogeneous deposits in DMT/PTA should be removed by filtration to a fineness range between 1 and 2 μm . Most of the earlier plants were based on the DMT route, since high purity commercial grade PTA was not available during those days.

Nowadays the PTA route is increasingly followed for the production of PET. The PTA route has many advantages over the DMT route. They are:

1. PTA gives higher production output to about 15 per cent higher, due to the faster rate of esterification and reduced raw material weight to product ratio.
2. Capital investment to construct a polyester fibre plant based on PTA is at least 20 per cent less than one based on DMT route.
3. PTA has higher bulk density than DMT and hence requires less storage space compared with DMT.
4. The PTA process needs less MEG as compared with DMT (1:1.15 vs. 1:2). Thus less MEG is to be recovered during polycondensation resulting in lower investment for MEG recovery and recycle system. This in turn promotes energy conservation.
5. PTA process is safe, as methanol is not evolved during esterification while in DMT process; methanol is produced as a by-product. Methanol is highly inflammable and can cause explosion so the system should have explosion proof equipment, which adds to capital cost in DMT process.
6. Small amount of catalyst is used in PTA process. As a result, a much cleaner polymer is obtained, which gives better colour of polymer, higher spin pack life in spinning and lower breakages in stretching and better clarity to containers/bottles.
7. Higher molecular weight is reached in less time in the PTA process than with the DMT process.

Drawback of PTA process is that handling is difficult since PTA does not melt at suitable temperature, nor it is soluble in solvent whereas DMT melts at 140°C and can be easily pumped (or) transferred in molten form. In the case of the PTA process, the reaction proceeds in heterophase due to its poor solubility in MEG, leading to non-uniformity in the product from batch to batch. Hence, efficient stirring during esterification is required. Further PTA process produces higher amount of DEG, a side-reaction product catalysed by acidic medium, than DMT route.

Formation of PET consists of two main reactions namely: (i) esterification (or) precondensation and (ii) polycondensation. The esterification reaction is conducted in excess of MEG. The first step produces a prepolymer which contains bis(hydroxyethyl terephthalate) (BHET) (or) diethylene glycol terephthalate and short chain oligomers and by-products namely water (or) methanol depending upon the raw material used namely PTA or DMT respectively. In the case of the PTA route, the operating temperature was 240–265°C and pressure was 0.4 MPa during precondensation. In order to expedite the rate of polycondensation, a catalyst such as antimony

Table 1.5 Antimony free catalysts

Chemical base	Trade name	Company	Ref.
Titanium	Ecocat T	Zimmer AG	(Otto 2002)
Titanium + Phosphorus	Ecocat B	Polytrade	(Otto 2003)
Titanium complexes	Vertec C400	Johnson Matthey (formerly Syntex)	(Naylor 1997)
Titanium – Phosphorus complexes	Vertec AC 310		
Tetra-isopropyl Tetra-n-butyl titanate	Tyzor TPT Tyzor nBT	Invista/DuPont	(Duan 2002) (Lustig and Burch 1999)
Titanium – Silicon	C94	Accordis	(Martl 1995)
Alkali titanate	Hombifast	Sachtleben Chemie	(Schmidt 1996)
Germanium	TG/19	Teck Cominco (formerly Meld Form)	(John 2001)
Aluminium		Toyobo	(Nakajima 2002)

acetate, antimony trioxide, germanium dioxide or titanium can normally be used. Catalysts other than antimony are listed in Table 1.5. In addition to catalyst, stabiliser namely phosphoric acid, phosphorus acid, trimethyl phosphate, triethyl phosphate should be used to stabilize metal ions such as manganese, zinc, calcium, etc. and deactivate them when used as transesterification catalyst. The most effective catalysts for the transesterification of DMT with MEG were the acetates of zinc, lead (II), mercury (II) together with cobalt (III) acetylacetonate and antimony trioxide (Yoda, 1970). A detailed review for esterification and transesterification reaction using titanium catalyst has been reported elsewhere (Siling, 1996). Theoretically, under such conditions, all chains should terminate with hydroxyl end groups. However, degradation reaction produces a certain amount of carboxyl end groups, which indicates the extent of degradation that had taken place in the melt.

In the polycondensation reaction, there are two chain growth reactions. They are: (i) polyesterification between chain ends with carboxyl and hydroxyl end groups with elimination of water and (ii) polytransesterification between hydroxyethyl end groups and ester end groups with the elimination of MEG, which predominates in the later stages of the reaction. Polycondensation was carried out in vacuum (0.13 KPa) at 275–290°C. At the end of polycondensation, the molten polymer was quenched in water to obtain strands, which were granulated into chips. IV obtained was in

the range of 0.5 to 0.7 dL/g and the residual acetaldehyde (AA) content was approx. 50 ppm.

Side reactions

Many side reactions take place during polymerization of PET. The important one is the etherification of MEG to form diethylene glycol (DEG). Up to 50 per cent of total DEG is generated during the initial stages of polycondensation in the preheating and another 40 per cent in the low vacuum state and remaining 10 per cent during the final vacuum stage (Renwen, 1983). Being a diol and less volatile, DEG gets incorporated as a comonomer in PET. In the PTA route, DEG is formed during the esterification step. Both alkali and alkaline earth metals as well as quaternary ammonium compounds can be used to bring about a significant reduction in the level of DEG formed. DMT route produces less DEG content than PTA route because high acidity of PTA catalyses the formation of DEG and this must be controlled at an acceptable level to give consistent polymer properties. The effect of increasing DEG content on PET properties leads to: (i) reduction in heat and light resistance; (ii) decrease in the glass transition and melting temperature; (iii) decrease in the hydrolytic thermal and oxidative degradation resistance; (iv) increase in the dyeability up to 1.5 to 2.5 per cent; (v) slowness in the crystallization kinetics; and (vi) increase in the softness and the breakage of pills. For textile applications, it is necessary to ensure that the DEG content is constant from batch to batch. Otherwise, it leads to non-uniform dyeing. The decrease in melting point (T_m) with respect to DEG content can be predicted with an accuracy of ± 1.5 per cent using the following equation:

$$T_m (\text{°C}) = 261 - (\text{wt. \% of DEG} \times 4.2)$$

DEG further loses water to form dioxane, which has higher vapour pressure and will be removed from the process as the column top product. Dioxane is formed when the DEG end group undergoes intramolecular reaction to form the terephthalic acid end group and dioxane (Hovenkamp and Munting, 1970).

Thermal degradation occurs during synthesis and processing at temperatures above melting point. As a result, the ester bond undergoes scission, leading to the terminal vinyl group and carboxyl end group, which then rearrange to form the AA. In packaging application, the AA migrates to the food content which affects the flavour of the food. The acceptable limit is <1 ppm. Another side reaction is the formation of cyclic oligomers, which occurs by ester interchange reaction in PET and cyclisation occurs mainly at the hydroxyl chain ends in the molten state (Cho *et al.*, 1998).

1.5.2 Solid state polymerisation

Pilati (1989) has published a comprehensive review on solid state polymerisation (SSP). To further reduce acetaldehyde content and increase molecular weight, the SSP is carried out for the amorphous chips. The advantages of choosing the SSP route rather than the melt phase route for further increasing the molecular weight are as follows:

1. problems associated with the stirring of the viscous melt are eliminated in the solid state;
2. lower investment and running costs of the continuous SSP route, which does not require very high temperatures and vacuum associated with the melt phase; and
3. degradation and side reactions were limited in SSP due to the lower processing temperatures used.

Before carrying out SSP, amorphous chips are crystallised in fluidised pre-crystalliser at about 170°C for 30 min with vigorous agitation to prevent sticking. The chips are further crystallised at 190°C in a rotary crystalliser, giving them a crystallinity of 30 per cent and density of 1.3845 g/cc. Then SSP is carried out by gravity flow continuous SSP reactor. SSP is operated in an inert gas stream or in a vacuum and an operating temperature of 180–240°C. Nitrogen gas is preferably used. IV of PET chips increased to 0.72–1.2 dL/g and the residual AA content was below 1 ppm.

It has been reported that the molecular weight correlates with the square root of the reaction time for both catalysed and uncatalysed SSP process (Jabarin and Lofgren, 1986; Droscher and Wegner, 1978). Rate of SSP reaction depends on many factors such as temperature and time (Jabarin and Lofgren, 1986), pellet size (Chen and Chen, 1987), crystallinity (Chang, 1970), additive types and concentration (Kokkolas *et al.*, 1995), process gas type and quantity (Hsu, 1967; Mallon *et al.*, 1998), molecular weight (Buxbaum, 1979) and end group concentration (Wu *et al.*, 1997). Ravindrath and Mashelkar (1990) developed a method for the typical industrial SSP process of PET. They concluded that the reaction rate decreases by a factor of 6 for the temperature range between 285 and 220°C accompanied by a decrease of the thermal degradation by a factor of 40.

The SSP process can be eliminated, if an integrated process such as the direct high IV (DHI) process (or) melt-to-resin (MTR) technology is followed. DHI and MTR technologies were developed by Zimmer and Uhde Inventa with Fischer respectively. The integrated process gives economic advantage due to reduced investment and conversion cost, reduced raw material consumption and better/comparable chip quality. Table 1.6 shows the comparison of PET resin quality produced by MTR and SSP process.

Table 1.6 Comparison of MTR and SSP processes

Processes	Unit	MTR®	SSP
Resin IV	dL/g	0.65–0.85	0.75–0.82
IV tolerance		±0.008	±0.02
ΔIV core/shell		0	>0.03
Precursor COOH ^a	meq/kg	50–70	30–40
COOH ^a	meq/kg	<25	<30
Melting point ⊗	°C	248–252	248–252
Colour b* ⊗	CIE Lab	<+1.0	<+1.0
Crystallinity	%	<35	>50
Heat of fusion	J/g	42–48	>50
Polydispersity		1.8	2.4

Note:

^aDepends on the recipe

Uhde Inventa Fischer claims that MTR can render a benefit of €30 to €40 on conversion costs compared with older conventional continuous plants.

1.5.3 Properties

Polyesters have good resistance to most mineral acids but concentrated sulphuric acid dissolves polyesters with partial decomposition. Polyesters display excellent resistance to conventional bleaching agents, cleaning solvents and surfactants and the degree of crystallinity and molecular orientation determines the extent of resistance. Basic substances attack polyester fibres in two ways. Strong alkalis cause dissolution of the fibre surface. Weak bases such as ammonia and other organic bases such as methyl amine penetrate into the non-crystalline regions of the structure. Because of the lack of chemical dye sites, polyester fibres are usually dyed with disperse dyes such as amacron, artisil, calcosperse, cekryl, celliton, disper-sol, duranol, esterophile, foron, genecron, harshaw ester, latyl, palanil, polydye, resolin, samaron, setacyl, terasil, etc. Polyester fibres are dyed from an aqueous bath at above 100°C or by the use of a carrier such as biphenyl, phenyl salicylate. The rate of dyeing polyester fibres is slower than that of cellulose triacetate or acetate.

Intrinsic viscosity (IV) is a measure of molecular weight and that determines the end use of PET. Solvents such as *o*-chlorophenol, 60:40 phenol/tetrachloroethane and 50:50 phenol/1,2-dichlorobenzene are typically used to determine IV of PET resin. IV is correlated to the molecular weight by the well-known empirical relationship proposed by Mark and Houwink:

$$[\eta] = K * \bar{M}^\alpha$$

where η is IV, \bar{M} is the molecular weight and K and α are constants, which are solvent dependent. Depending upon how the co-relationship was established M can be expressed as, number average molecular weight (\bar{M}_n), weight average molecular weight (\bar{M}_w) and viscosity average molecular weight (\bar{M}_v).

Ravens and Ward (Ravens and Ward, 1961) have established the above relationship using *o*-chlorophenol at 25°C by end-group analysis.

$$[\eta] = 1.7 \times 10^{-4} * \bar{M}_n^{0.83}$$

Melt viscosity (low shear) of PET can be predicted from the IV, which was measured using *o*-chlorophenol, using the formula

$$\eta_0 = 0.129 [\eta]^{5.35} \exp \{6800/T\}$$

where η_0 is the Newtonian melt viscosity (poise) and T is the absolute temperature.

When GPC was used the above relationship changed as follows:

$$[\eta] = 1.47 \times 10^{-4} * \bar{M}_w^{0.768}$$

$$[\eta] = 4.68 \times 10^{-4} * \bar{M}_w^{0.68}$$

In the above relationships, IV solvents used were *o*-chlorophenol and 60:40 phenol/tetrachloroethane at 25°C (Moore, 1960) respectively.

IV values of 0.40, 0.63, 0.72 and 1.0 dL/g correspond to number of average molecular weights of approx. 10000, 18000, 24000 and 40000 g/mol respectively. IV of fibre grade is in the range of 0.40 to 0.70 dL/g and yarns in the range of 0.72 to 0.98 dL/g. Recommended IV of various fibre types are given in Table 1.7. IV of bottle grade is in the range of 0.70 to 0.85 dL/g. IV of biaxially oriented film and thermoforming sheet grades is in the range of 0.60 to 0.70 dL/g and 0.7 to 1.0 dL/g respectively. IV of

Table 1.7 IV data of different types of PET fibre/yarn

Types of fibre/yarn	IV (dL/g)
Low pill staple fibre	0.40–0.50
Wool type fibre	0.58–0.63
Cotton type fibre	0.58–0.64
Carpet fibre	0.60
High Tenacity Cotton type fibre	0.63–0.70
Technical yarn	0.72–0.90
Tyre-cord yarn	0.85–0.98

Table 1.8 Unit cell parameters of PET

a (nm)	b (nm)	c (nm)	α (°)	β (°)	γ (°)	ρ_{crystal} (g/cc)	Ref.
0.554	0.414	1.086	107.5	112.2	92.2	1.471	(Astbury, 1946)
0.456	0.594	1.075	98.5	118	112	1.455	(de Daubeny, 1954)
0.452	0.598	1.077	101	118	111	1.479	(Tomashpolskii, 1964)
0.448	0.585	1.075	99.5	118.4	111.3	1.515	(Fakirov, 1975)
0.444	0.591	1.067	100.1	117	111.8	1.515	(Asano, 1999)
0.452	0.592	1.070	99.8	117.5	111.4	1.479	(Hall, 1984a)
0.448	0.588	1.071	100.1	117.9	110.7	1.501	(Heuval, 1978)
0.450	0.590	1.076	100.3	118.6	110.8	1.501	(Kinoshita, 1979), (Kitano, 1995)
0.462	0.592	1.068	99.8	127.6	104.9	1.578	(Liu, 1997a)

fibre grade is usually in the range of 0.40 to 0.98 dL/g and this fibre grade may contain 0.03 to 0.4 wt. % of titanium oxide (TiO_2) as delustring agent.

Table 1.8 shows the crystalline data of PET. Heat of fusion values reported for crystalline PET are generally in the range of 22.6 and 27.8 kJ/mol. Polyethylene glycol (PEG) with different molecular weights is added to enhance the dye receptivity of PET fibres. Like most materials, PET tends to produce small crystallites when crystallised from an amorphous solid, rather than forming one large single crystal. Light tends to scatter as it crosses the boundaries between crystallites and the crystalline PET is opaque and white in most cases. Fibre drawing is among the few industrial processes that produces a nearly single crystal product. PET fibre when exposed to elevated temperatures for 28 days in air, 90 and 30 per cent of strength retained at 150 and 200°C respectively, whereas exposure for seven days in pressurised steam retains 90 per cent of strength at 100°C and 0 per cent at 150°C.

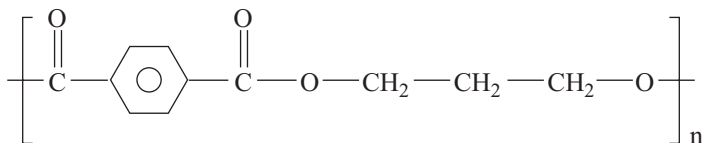
1.5.4 Applications

PET grades with relatively higher molecular weights are used for making industrial filaments, which can be either thick for rubber tyres, conveyor belts, seat belts, hoses and ropes, coated fabrics, etc. or relatively thinner for sewing threads, light-weight coated fabrics, etc. Staple fibre finds major use in making blended fabrics, low denier fibre for blending with cotton and coarser fibre for blending with wool. Fabrics made from PET POY

microfilaments are breathable and water-repellent with soft drape and pleasant feel.

1.6 Poly(trimethylene terephthalate) (PTT)

Poly(trimethylene terephthalate) (PTT) is otherwise known as poly(propylene terephthalate) (PPT). PPT nomenclature does not distinguish whether the glycol moiety is derived from branched 1,2-propane diol or linear 1,3-propane diol. The PTT abbreviation is more popular and widely used than PPT. It is also known as 3GT. The repeat unit molecular weight is 206. Futura Polyesters Ltd is the first company outside USA to produce PTT resin. Shell chemical company and DuPont's PTT fibres are commercially known as Corterra™ and Sorona™ respectively. PTT is prepared from DMT (or) PTA and 1,3-propane diol (PDO). PTT has been a recent addition to the list of commercial aromatic polyesters, even though it was first synthesized by Whinfield and Dickson in 1941 (Whinfield and Dickson, 1946). PTT can be processed by extrusion, injection moulding, blow moulding and melt-spinning and the molten polymer has good melt strength. Chemical structure of PTT is as follows:



PTT had never gone beyond academic interest until recently, because PDO was very expensive initially, selling at about \$20 per kg. PDO was first marketed by Degussa AG as a fine chemical and was synthesized from acrolein by selective hydration under pressure at 50°C using acid catalyst followed by hydrogenation using Raney Nickel as catalyst. Later, Shell invented an attractive less expensive route in which ethylene oxide is hydroformulated into 3-hydroxy propanol by using synthesis gas (a mixture of carbon monoxide and hydrogen) and cobalt as catalyst. Then 3-hydroxy propanol aqueous solution was concentrated and hydrogenated to produce PDO. Recently, DuPont has announced that PDO based on biochemical route using corn starch as feed stock will be commercialized in 2007.

1.6.1 Polymer production

Similar to PET production, PTT can be produced by polycondensation reaction through the DMT (or) PTA route. PTT can be produced by the

transesterification of PDO and DMT in the melt at 180–200°C using a zinc acetate dehydrate catalyst. After the completion of precondensation, the temperature was raised to 265°C and the melt was polymerised under vacuum of <0.3 mm of Hg using a titanium butoxide catalyst. Because of the lower reactivity of PDO, a more active catalyst such as titanium or tin is needed for PTT. Undesired side reactions occur, during both precondensation and polycondensation reactions, leading to the formation of acrolein, allyl alcohol, dipropyl glycol and cyclic dimer by-products. Among these acrolein is a very strong lachrymator, which can irritate lung and respiratory tracts and affect breathing. The US Occupational Safety and Health Agency industrial hygiene guidelines gave the time-weighted exposure limit of acrolein over a period of 8 h as 0.1 ppm, while the short-term exposure limit for 15 min is 0.3 ppm.

PTT should be dried to a moisture level of <30 ppm, in a close-loop hot air dryer having a dew point preferably lower than –40°C at 130°C for four hours. Otherwise, hydrolytic degradation will take place during melt processing. The dried polymer can be extruded at 250–270°C into bulk continuous filaments (BCFs), partially oriented yarn (POY), spin-draw yarn (SDY) and staple fibre. Because of its low T_g, PTT fibres and fabrics are disperse dyed at atmospheric boil without the need of a carrier (Traub *et al.*, 1995). PTT dyed at atmospheric boil has very good colour fastness against light, ozone and NO_x, similar to PET (Chuah *et al.*, 1995; Yang *et al.*, 1999).

1.6.2 Properties

PTT's excellent stress recovery property is similar to that of nylon and this makes PTT an excellent candidate for textile applications. When compared with other polyesters, PTT has a very good tensile elastic recovery property, which descends in the following order: PTT > PBT > PET (Ward, 1976). PTT is not readily soluble in solvents, which are commonly used for amorphous PET, because of its rapidly crystallising nature. However, PTT is readily soluble in stronger solvents such as hexafluoroisopropanol (HFIPA) (or) in a 1:1 mixture of trifluoroacetic acid and dichloromethane at room temperature. With care, when heated to 110°C, PTT dissolves in a 60:40 mixture of phenol/tetrachloroethane (Chuah, 2001). The IV of fibre producing pellets is 0.92 dL/g and the corresponding molecular weight is 48700 and polydispersity is 2. PTT is extrusion spun. Like PET, PTT is sensitive to hydrolysis degradation and should be dried before processing. Unlike PET, there is no need to crystallise PTT chips before drying. A typical fibre grade PTT has a melt strength of about 200 Pa-sec at 260°C and at a shear rate of 200 per sec.

Table 1.9 Unit cell parameters of PTT

PTT Dimension	(Dandurand, 1979)	(Desborough, 1979)	(Yang, 2001)	(Tadokoro, 1979)
a (nm)	0.4637	0.4620	0.453	0.458
b (nm)	0.6226	0.6200	0.6150	0.622
c (nm)	1.864	1.830	1.861	1.812
α (°)	98.4	98.0	96.87	96.9
β (°)	93.0	90.0	92.21	89.4
γ (°)	111.5	112.0	110.97	111.0
ρ_{crystal} (g/cc)	1.387	1.427	1.448	1.43

Contrary to the widely believed concept that aromatic polyesters with odd numbers of methylene units are more difficult to crystallise, PTT is fast crystallising. The rate of crystallisation is about an order of magnitude faster than PET. In terms of crystallising ability PTT is in between PET and PBT. Crystal density of PTT is 1.387 g/cc. Unit cell parameters are tabulated in Table 1.9. Unit cell of PTT is triclinic crystalline structure, each cell of which contains two chemical repeat units and the crystal space group is ρI (Dandurand *et al.*, 1979).

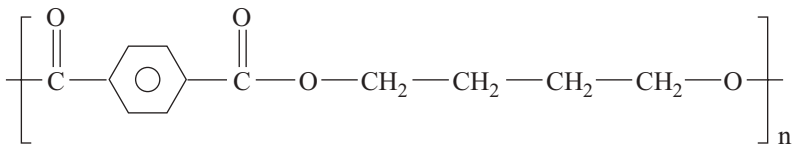
Hall has reviewed the crystal structures of PTT (Hall, 1984). Molecular configuration consists of rigid planar terephthaloyl moieties alternating with more flexible trimethylene moieties. The O – CH₂ – CH₂ – CH₂ – O segment of the chain has a near *trans-gauche-gauche-trans* conformation. Studies by Ward (Ward *et al.*, 1976) showed that PTT had an elastic unit cell, the (002) crystal lattice spacing of PTT responded immediately to the applied stress and the deformation was reversible below its critical strain. The microscopic reversible crystal chain deformation was attributed to the PTT's three methylene units arranged in a highly contracted and a very compliant *gauche-gauche* conformation (Desborough *et al.*, 1979, Poulin-Dandurand *et al.*, 1979). PTT was found to have a very low X-ray crystal modulus of 2.59 GPa compared with 107 GPa of PET. The heat of fusion of 100 per cent crystalline PTT as measured by Pyda *et al.* (1998) is 30 kJ/mol, which is in good agreement with the values reported by Gonzalez *et al.* (1988a). Based on the DSC measurements, melting point is reported to be at 237°C (Pyda *et al.*, 1998) and glass transition temperature is reported to be in the range of 37–45°C and melting point (Pyda *et al.*, 1998; Gonzalez *et al.*, 1988a) whereas higher glass transition temperature (59–69°C) was observed in dynamic mechanical analysis (DMA) studies. Other transitions observed are β at –70°C and γ at about –120°C (Gonzalez *et al.*, 1988b).

1.6.3 Applications

PTT carpets (Chua, 1996) showed excellent resiliency in walk test experiments, equivalent to nylon and much better than both PET and polypropylene. The high resilience characteristic of PTT is due to its unique crystal structure, which is very spring-like in its long axis. Further, it had a lower static charge of <3.5 kV, and was resistant to coffee, mustard, butadiene, red acid dyes and other stains (Chua, 1996). PTT is used in ready-to-wear, stretch apparels (Heschmeyer, 2000), active-wear, intimate apparels and inner linings, automotive and home upholstery. PTT monofilaments can be used to make paper forming fabrics, which find use in papermaking machines (Hsu, 1992). PTT is also used to make non-woven (Asahi Chemical Industry Co. Ltd, 1999) fibres, artificial leather (Goto and Muraoka, 1999), zip fasteners (Kawase and Kuratsuji, 1976), umbrella fabric (Yamamoto, 1999), racket guts and musical bowstrings (Oue and Yamaziki, 2000), pantyhose (Hiraga and Sonoda, 1999), cheese packaging (Kato and Fujimoto, 1999), hook-and-loop fasteners (Ohira, 1999), magnetic recording discs (Hosoi, 1988), electrical connectors (Hironaka and Suzuki, 1999) and flexible transparent film.

1.7 Poly(butylene terephthalate) (PBT)

Poly(butylene terephthalate) (PBT) belongs to aromatic polyester family. It is otherwise known as polytetramethylene terephthalate or 4GT. This thermoplastic polyester is prepared by polycondensation of 1,4-butane diol (BDO) with PTA (or) DMT. The repeat unit molecular weight is 220. PBT was brought to market by Celanese in late 1960s. Structure of PBT is given below:



PBT differs only slightly from PET in chemical composition but more substantially in its properties such as higher crystallisation rate and lower melting point. PBT fibres are manufactured by Zimmer and Ticona in the name of Celanex®. PBT resin is similar to polyamide resin nylon 6 in many aspects such as: (i) ability to crystallise quickly; (ii) good solvent resistance and mechanical properties; and (iii) similar melting point. PBT is different from nylon 6 with respect to moisture absorption. PBT absorbs less moisture than nylon. PBT shows more resistance to staining than nylon and can

be coloured by the use of pigments. However PBT is more difficult to colour by solution dyeing than nylon.

1.7.1 Polymer production

PBT production is similar to PET and can be produced by polycondensation reaction from DMT (or) PTA and BDO. In PBT production, THF is formed as by-product by irreversible acid-catalysed dehydration of BDO. Alternatively, THF is produced by back-biting process. DMT route produces approx. 6 mol. % and PTA route 13 mol. % of THF (Schumann, 1990). Formation of THF is minimised by the addition of 2–8 per cent of water to PTA and BDO (US Patent 3,936,421), the usage of combination of titanium and tin catalysts (US Patent 4,014,858), the usage of titanium catalyst (US Patent 5,015,759), the slow addition of PTA (US Patent 4,329,444), or the addition of a portion of BDO at a later stage of reaction (US Patent 4,565,241) or carrying out polycondensation before PTA is exhausted (US Patent 4,364,213). The other by-product formed is 1,3-butadiene. In melt phase, \bar{M}_n of 20000 to 35000 is achieved and is used for both fibre and engineering plastics applications. SSP is used to increase the molecular weight to 40000, which is suitable for certain injection moulding and extrusion applications. After polycondensation, i.e., before SSP, PBT resin is already crystalline and opaque and therefore, unlike PET, there is no need to precrystallise PBT resin in a fluid bed. Due to lower melting point (225°C), SSP is carried out at 180 to 200°C. Even though PBT is less sensitive to oxidation than PET, SSP is carried out in nitrogen. Reaction rate of PBT is faster than that of PET, IV is increased from 0.8 to 1.2 dL/g in about 12 hours.

1.7.2 Properties

PBT displays good solvent resistance, high heat resistance, good elongation, high strength and modulus, excellent electrical properties, high gloss, good inherent lubricity and wear resistance. Density of amorphous PBT is in the range of 1.265–1.268 g/cc and that of crystalline is 1.395 g/cc. Melting point and glass transition temperature of PBT are 225°C and 25°C respectively. Heat of fusion for crystalline PBT is 32 kJ/mol (Cheng *et al.*, 1988). Under moderate conditions, the degree of crystallinity is about 35 to 40 per cent. Water absorption is less than 0.1 per cent after 24 h. However, PBT is not recommended for extended use in water/aqueous solution above 52°C. PBT is intrinsically resistant to detergents, weak acids and bases, aliphatic hydrocarbons, fluorinated hydrocarbons, alcohols, ketones, MEG, carbon tetrachloride, oils and fats at ambient temperature.

Table 1.10 Unit cell parameters of α -form of PBT

PBT Dimension	α -form (Bornschneggl, 1980)	α -form (Hall, 1976)	α -form (Joly, 1975)	α -form (Liu, 1997)
a (nm)	0.482	0.489	0.487	0.494
b (nm)	0.593	0.595	0.596	0.598
c (nm)	1.174	1.167	1.171	1.156
α (°)	100	98.9	100.1	99.8
β (°)	115.5	116.6	116.6	116.5
γ (°)	111	110.9	110.3	111.15
ρ_{crystal} (g/cc)	1.403	1.392	1.396	1.397

Table 1.11 Unit cell parameters of β -form of PBT

PBT Dimension	β -form (Yokuouchi, 1976)	β -form (Desborough, 1977)	β -form (Grasso, 1989)	β -form (Hall, 1976)
a (nm)	0.473	0.473	0.473	0.469
b (nm)	0.575	0.583	0.588	0.580
c (nm)	1.311	1.290	1.306	1.300
α (°)	104.2	101.9	103.3	101.9
β (°)	120.8	119.4	119.8	120.5
γ (°)	100.9	105.1	104.4	105
ρ_{crystal} (g/cc)	1.33	1.33	1.32	1.36

Among the aromatic polyesters, PBT has high crystallisation rate next to PBN, about an order of magnitude faster than PTT, which in turn is an order of magnitude faster than that of PET (Chuah, 2001). Similar to PTT, PBT has triclinic crystalline structure. Two types of triclinic structures exist namely α - and β -form, which are reversible. Unit cell parameters of α -form and β -form of PBT are set out in Tables 1.10 and 1.11. In the non-extended state, the α -form prevails with *gauche-trans-gauche* conformation of butylenes moiety. The β -form exists in the extended state with all *trans* conformation depending on the drawing condition. Unit cell volume of α - and β -forms of PBT are 0.261 and 0.267 nm³.

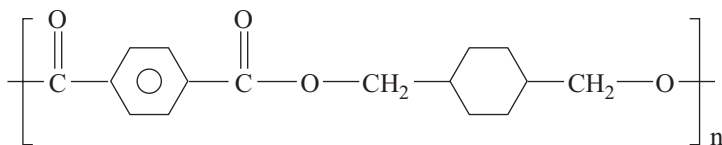
1.7.3 Applications

PBT is used for textile applications due to its stretchability and improved dyeability. PBT fibres are used as tooth brush bristles, carpet yarn and sports wear, and in apparel, underwear and hosiery. It is also used for swim

wear since it has high tenacity, stability and good resistance to chlorine. PBT is preferably used for the production of engineering plastics due to its combination of dimensional stability, tensile strength, increased flexibility and fast crystallisation rate. PBT resins are used in drapery hardware, pen barrels, heavy duty zippers, hair dryers, pocket calculators, iron and toaster housings and food processor blades.

1.8 Poly(1,4-cyclohexylene dimethylene terephthalate) (PCT)

Poly(1,4-cyclohexylene dimethylene terephthalate) is abbreviated as PCT. It is prepared from 1,4-cyclohexanedimethanol (CHDM) and PTA (or) DMT. CHDM imparts the following advantages for polyester resins: (i) higher T_g ; (ii) higher reactivity; (iii) glossiness and transparency; and (iv) shock resistance and flexibility. However, it also imparts certain disadvantages for polyester resins such as: (i) higher viscosity; (ii) lower solvent solubility; and (iii) lower tendency to crystallise. Chemical structure of PCT is as shown below:

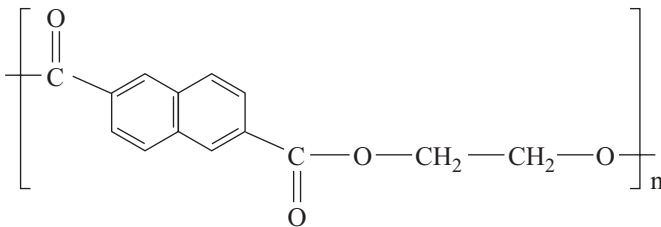


Unlike other glycols, CHDM exists in *cis* and *trans* forms. The *cis* form imparts increased gas barrier property when compared to *trans* form. PCT is less dense than PET so it offers great bulk. Specific gravity of PCT is 1.23 whereas for PET it is 1.38. PCT provides softness inherent to the molecular composition. PCT offers better release properties than PET which means that it is reusable and washes and cleans up easily. PCT has better hydrolytic stability than PET so it withstands better the rigours of repeated washing and sterilization. PCT has a higher melting point than PET (290 vs. 250°C). PCT has higher glass transition temperature than PET (88 vs. 80°C). Heat distortion temperature of PCT is 75 and 65°C at 0.455 and 1.82 MPa respectively. PCT has better chemical resistance to auto fluids and printed circuit board cleaning chemicals than PET. PCT is sold under the trade name of Kodel II by Eastman Chemical Products Inc. PCT fibres can be used for high temperature applications, for example autoclave and industrial applications such as filtering, insulation, etc. Because of its superior softness with resilience, PCT fibres can be used for pillows, cushions, bed pads, carpets, etc. The safe ironing temperature for

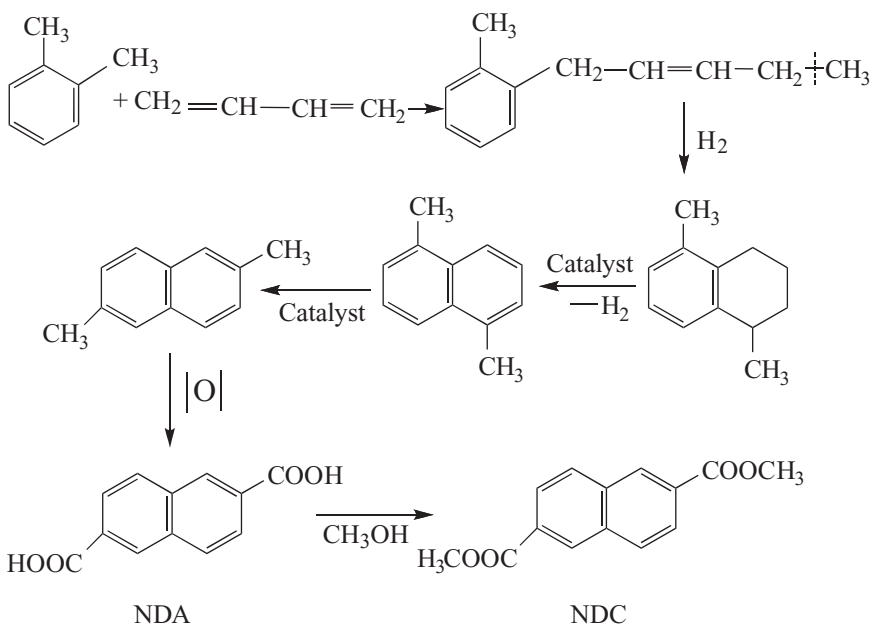
PCT based clothes is 205°C whereas for PET it is 145°C. PCT fibres shrink less than PET fibres. Percentage shrinkage at 190°C (air) are <1 and <6 for PCT and PET fibres respectively. Percentage shrinkage at 100°C (water) for PCT fibres is <0.5 and for PET fibres is <1. PCT fibre has better resiliency than PET, without compromising high temperature resistance. It competes successfully against nylon in the carpet yarn market. The higher HDT has allowed PCT to carve out a niche market in surface mount components, electrical connectors, sensors and switches, especially those which require IR oven compatibility.

1.9 Poly(ethylene 2,6-naphthalate) (PEN)

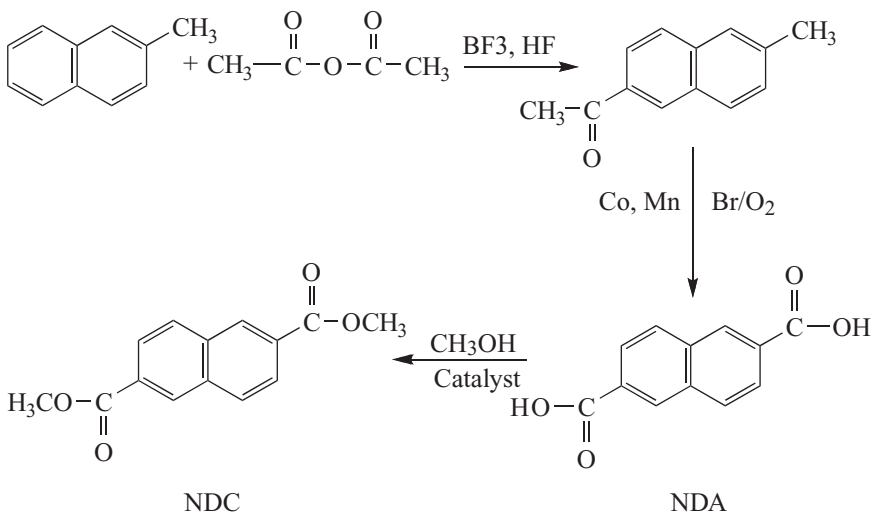
The expansion of PEN is poly(ethylene 2,6-naphthalate) and is three times more expensive than its analogue, PET. The systematic nomenclature of PEN is poly(oxy-1,2-ethanediyloxycarbonyl-2,6-naphthalenedicarbonyl). Several other poly(ethylene naphthalate)s such as poly(ethylene naphthalene 1,8-dicarboxylate) (Sakai *et al.*, 1992; Yokota, 1994), poly(ethylene naphthalene 2,7-dicarboxylate) (Khanna *et al.*, 1994; Sullivan and Hoyt, 1996), poly(ethylene naphthalene 1,5-dicarboxylate) (White *et al.*, 1999) are reported. NDC has been commercially available from British Petroleum since 1996. Teijin Ltd of Japan has manufactured PEN for its own uses in films since 1973. In the late 1980s, both Eastman Chemicals and Goodyear developed PEN. Eastman's PEN was called 5XO (five times better oxygen barrier than PET) and Goodyear's PEN was called HP (high performance). Performance Fibers manufactures PEN fibres under the name of PenTec®. Futura Polyesters Ltd makes PEN with different IVs ranging from 0.45 to 0.85 dL/g. The chemical structure of PEN is:



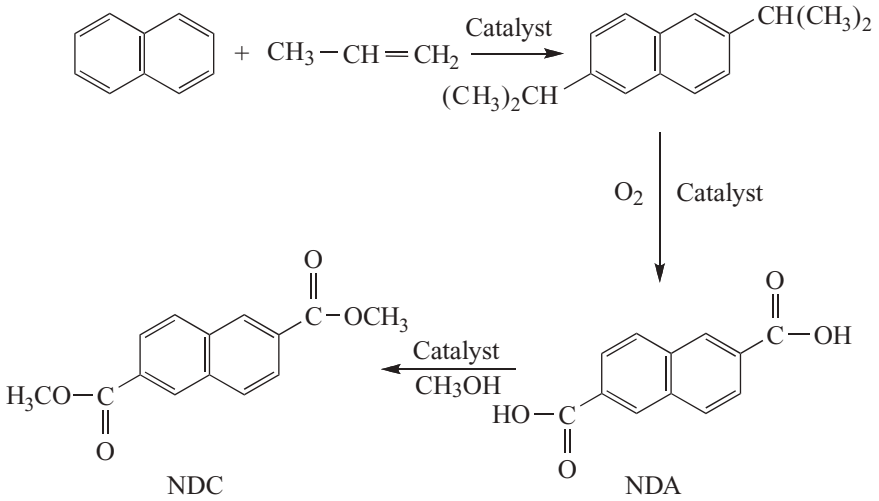
NDA/NDC can be synthesized from various raw materials (Shikkenga and Wheaton, 1989, 1990; Jia and Sheng, 1999; Motoyuki *et al.*, 1999; Holzhauser and Young, 1993; Uchida and Marumo, 1989) as follows:

(a) from *o*-xylene and 1,3-butadiene

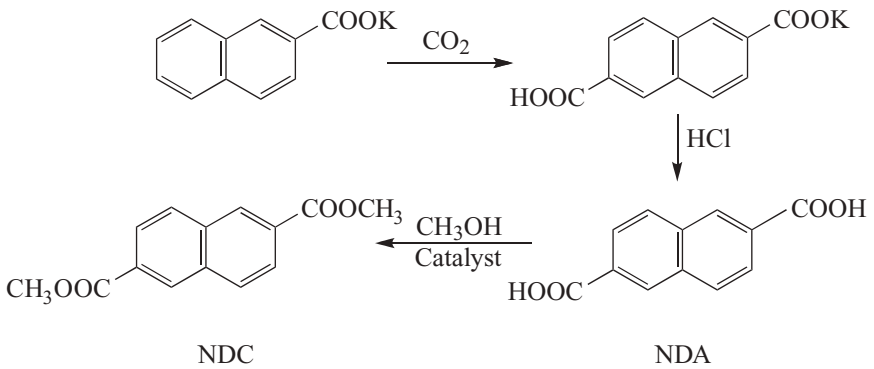
(b) from 2-methylnaphthalene and acetyl acetate



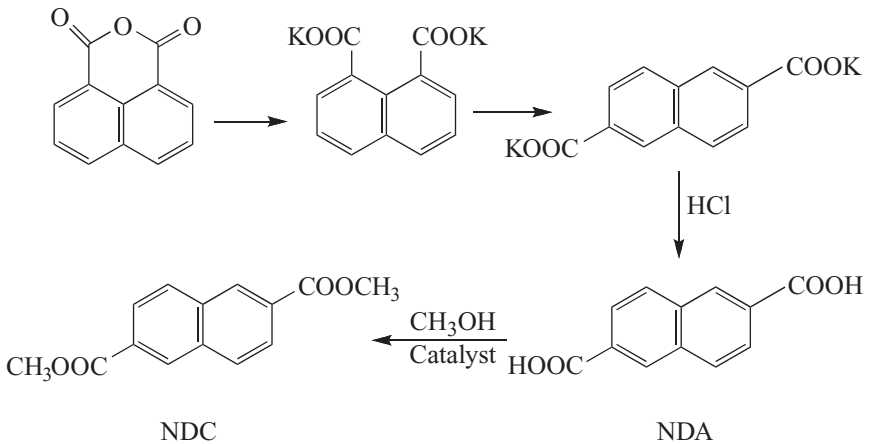
(c) from naphthalene and propylene



(d) from potassium naphthalene carbonate



(e) from 1,8-naphthalene dicarbonate



1.9.1 Polymer production

PEN can be prepared from MEG and NDC (or) NDA by polycondensation reaction. Alternatively, PEN can be prepared by ROP (Hubbard and Brittain, 1996) of cyclic PEN in the presence of a tin catalyst. Cyclic PEN is prepared by the reaction of di(chlorocarbonyl)-2,6-naphthalene with MEG (Brunelle and Bradt, 1993; Brunelle, 1994) in dichloromethane in the presence of diazabicyclo[2.2.2]octane.

1.9.2 Properties

Both glass transition and melting temperatures of PEN are higher than that of PET. PEN also exhibits an increased tensile strength, as well as elastic modulus and elongation at break. Both oxygen and carbon dioxide gas barrier properties are about 70–80 per cent increased compared with PET. Due to high melt viscosity, PEN needs a higher processing temperature during the melt extrusion process and is slow crystallising resin. Density of PEN is lower than PET.

Depending on the previous thermal history, PEN has two crystalline structures namely α - (Mencik, 1967) and β -forms (Buchner *et al.*, 1989), which are triclinic. When crystallisation temperature is $\leq 200^\circ\text{C}$, α -crystal is formed whereas the formation of β -crystal is at crystallisation temperature of $\geq 240^\circ\text{C}$. Their densities are 1.407 and 1.439 g/cc and that of amorphous material is 1.326 g/cc (Liu *et al.*, 1998). The α -form crystal structure has dimensions of $a = 0.651$ nm, $b = 0.575$ nm, $c = 1.32$ nm, $\alpha = 81.33^\circ$, $\beta = 144^\circ$ and $\gamma = 100^\circ$ whereas β -form crystal structure has dimensions of $a = 0.926$ nm, $b = 1.559$ nm, $c = 1.217$ nm, $\alpha = 121.6^\circ$, $\beta = 95.57^\circ$ and $\gamma = 122.52^\circ$.

The dielectric constant (ϵ) of PEN is lower than that of PET in the entire temperature range. PEN is more suitable for high temperature applications because $\tan\delta$ of PEN is higher than that of PET at room temperature, but is lower than those of PET at 90 and 130°C . PEN has greater chemical resistance than PET. Even though this is a desirable property for many applications, it makes PEN difficult to characterise by IV measurements, GPC, NMR and end-group analysis and this difficulty is even greater for highly crystalline material. Due to the extended chromophore group naphthalene, PEN absorbs UV light up to 380 nm whereas PET's absorption is up to 313 nm. This property helps to use PEN in packaging applications. A blue-white visible fluorescence results when PEN is excited by black light emitting at ~ 360 nm. This permits ready identification and separation of PEN from PET chips, containers, films and fibres (Ouchi *et al.*, 1976).

PEN begins to stick at 140°C as the T_g is at 121°C . But the crystallisation rate is not significant below 180°C and the maximum rate of crystallisation

is at 200°C. However, at a crystallisation temperature of about 200°C, it has a strong tendency to stick strongly in the presence of high moisture content. PEN expands and bursts; known as ‘popcorning’. PEN requires 22 h at 235°C, to increase IV from 0.55 to 0.75 dL/g. The Mark–Houwink relationship for PEN resin is as follows:

$$[\eta] = 2.317 \times 10^{-3} * \bar{M}_w^{0.514}$$

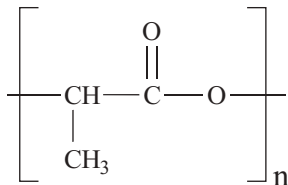
In the above relationship, the IV solvent was used and 60:40 phenol/tetrachloroethane at 30°C.

1.9.3 Applications

PEN monofilaments are used for paper making felts, where the higher modulus, temperature and hydrolysis resistance are required. PEN fibre is used to make high performance sail cloth in racing, in tyre cord and also for making narrow and broad woven fabrics. PEN has been successfully used to contain liquid anaesthetics.

1.10 Polylactic acid (PLA)

Poly(lactic acid) (PLA) differs from the previously discussed polyesters because PLA is based on renewable resources and is a biodegradable polymer. It is otherwise known as polylactide. The chemical structure of PLA is shown below:



It is produced from any starch or sugar containing raw material such as corn, cereals, cassava, sugar cane, etc. PLA can be used as packaging materials such as biaxially oriented films, extrusion sheets for thermoforming and plastic bottles, textile materials such as filaments, staple fibres and non-wovens and engineering plastics. Although PLA is expensive it will become cheaper than PET, now that the crude oil price has risen above US\$80 per barrel. Depending upon the content of L and D isomers in PLA, melting point ranges from about 150°C to 210°C. Even though the polymer chain contains no aromatic rings, the steric hindrance of the pendant methyl groups gives some rigidity and thermal stability. Fibre elasticity and resiliency of PLA is similar to PTT or PBT and is attributed to the partial coiling of the backbone chain in the crystalline form.

1.10.1 Production of PLA

Production consists of two stages. During the first stage, glucose is fermented to produce lactic acid and in the second stage, lactic acid is polymerized to PLA. Fermentation of glucose produces not only lactic acid, in the form of sodium lactide but also numerous impurities such as proteins, cellular mass, etc. Sodium lactide is purified and converted into lactic acid. For polymerizing lactic acid, excellent purity is a requisite. Lactic acid undergoes polycondensation to form oligomer, which is thermally depolymerised to cyclic dimer namely dilactide. ROP of dilactide produces PLA and about 5 per cent of non-convertible dilactide, which is removed by applying a vacuum. Otherwise, rapid hydrolytic degradation takes place.

1.11 World market

Many manufacturers of raw materials have already installed (or are planning to schedule) their manufacturing units and the list is given in Tables 1.12 and 1.13 for PTA and MEG respectively. Many polyester manufacturing plants have started production recently and many more are scheduled to start production in the future. These manufacturers are listed in Table 1.14. Global polyester capacity greatly exceeds consumption. With the

Table 1.12 Some of the new manufacturers of PTA in Asia

Company	Location	Technology	Capacity KTA	Year
Indian Oil	India	Invista	600	2006
Mitsubishi Chemical	China/India	MCC	600/800	2007/2009
Yisheng	China	Invista	600	2005
Sanxin	China	Eastman/Invista	1800	2005/2006
SMPC	Thailand	Mitsui	500	2005
Indorama	Thailand	Invista	640	2006
NPC	Iran	MCC	350	2006
OPC (FET)	China	Invista	600	2006
Reliance	India	Invista	600	2006
Yangzi	China	Invista	600	2007
BP Zhuhai	China	BP	900	2008
DaHua	China	Hitachi/Tuntex	1500	2010
Zinan	China		530	2009
Liaoyang	China	Invista	600	2006
Taekwang	Korea	Technimont	500	2007
Xianglu	China	Hitachi/Tuntex	1500	2009
Jialong	China	Invista	600	2009
Hanbang	China	Invista	600	2010

Table 1.13 Some of the new manufacturers of MEG in Asia

Company	Location	Capacity KTA	Year
ShangHaiPC	China	320	2007
Nanya	Taiwan	700	2007
NPC	Iran	800	2007
TOC	Thailand	100	2008
Liaoyang	China	200	2008
Aramco	Saudi	600	2008
Sharq	China	700	2008
Lotte Daesan	Korea	400	2008
Equate	Kuwait	600	2009
Yansab	Saudi	700	2009
Shell	Singapore	750	2009

Table 1.14 Some of the recent PET manufacturers and their capacity

Company	Location	Capacity KTA	Year
PCH (Neo Gr)	Lithuania	150	2005
FET	China	160	2006
Wellman	USA	130	2006
Senezh (Europlast)	Russia	80	2006
Invista	Mexico	210	2006
Indorama	Lithuania & USA	175 & 80	2006
DAK	USA	200	2007
Voridian	USA	350	2007
NPC	Iran	140	2007
M & G	Brazil	450	2007
Sabic	Saudi Arabia	250	2007
Sanfangxiang	China	300	2007
W. B. Radici	China	200	2008

exception of South America and Western Europe, all other regions produce more polyester than they consume, leading to a surplus of 4 million MT.

In 1997, the crude oil price was about \$25/bbl and since then the price has passed \$80/bbl. In the late 1990s, the polyester price was about \$800/MT and had risen to \$1200/MT at the time of writing. The tripling of the crude oil price has not proportionally increased the polyester price and the increase is only 50 per cent. The newly constructed fully integrated plants and increased competition among the polyester manufacturers has reduced the overheads and squeezed the profit of polyester manufacturers.

Many polyester industries are expected to emerge in the next couple of years, from the Middle East, China and India. Further polyester industry

growth is limited by low returns; and escalating construction costs and salaries due to a shortage of experienced and skilled manpower. Even with the above constraints, polyester capacity is expected to grow from 18.8 million MT in 2007 to 22.7 million MT in 2010. About 4 to 5 per cent growth is estimated during the next five years in the textile industry and about 8 per cent in packaging applications.

1.12 Future trends

Among polyesters, PET will continue to be in the leading position for applications in packaging and textiles with more applications in 'Technical Textiles' in sectors of agriculture, building, geo, home, medical, packaging, etc. Also there will be more developments in textile applications for comfort, sportswear, etc. The global production of technical fibres is growing by 13 per cent with applications in the aerospace industry including space and defence. Quality improvements such as increased barrier capabilities, softness and loft will be further improved. An increased demand for renewable raw materials and disposable materials for environmental and cost reasons will be a central issue in the future. Growth in today's booming markets will be influenced by a shortage of raw materials and energy. Polyester will continue to find newer applications because of its undisputable performance and properties.

At the current consumption rates, the current world crude oil reserves will be exhausted by the year 2043, unless new oil stocks are discovered. If, as predicted, the global population doubles in the next 50 years, the requirement for polyester resin at the current usage rate will also double. This will have a huge bearing on crude oil consumption. Therefore, the future of the polyester industry, in particular commodity resin, depends on how effectively the industry recycles polyester scrap and how quickly the industry moves from oil-based resources to renewable resources. The effective recycling of polyester resin will also reduce carbon dioxide emission, which in turn will minimise global warming. Even though, with the available technology today, one can make PDO and PLA using renewable resources, commercial production and effective utilisation have not yet taken full effect. PLA will become cheaper only when the crude oil price goes above \$80/bbl. Till then, PLA will be only of academic interest, unless new technology is invented to make polyesters from renewable resources.

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1.14 Sources of further information and advice

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2.1 Introduction

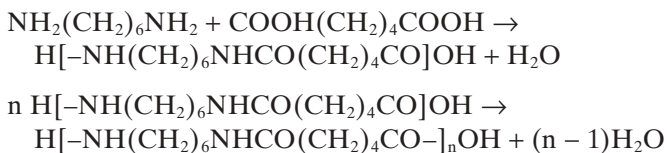
Nylon is a generic word representing a class of polymers as polyamides. Nylon was a product of a basic research started by Wallace Corothers at DuPont in 1928. The polymer age really started when the new synthetic nylon fiber was introduced in the market in 1938. Nylon captured public imagination, as four million pairs of nylon stockings were sold in the first few hours of sale on May 15, 1940. During World War II, nylon fabrics were used as waterproof tents, lightweight parachutes among other things. In the process an important principle was established that it is possible to chemically link hundreds of simple molecules of a kind or more, to make polymers with unique set of properties. One interesting example is the ability of molten polymer undergoing large deformations, which allows continuous production of fine filaments from thicker extrudates and this property of deformation is in turn connected to cumulative interactions of long chain polymeric molecules.

The word nylon was introduced to signify the fineness of the filament i.e. a pound of nylon could be converted to the length equal to the distance between New York (NY) and London (LON). A variety of polyamides are presently manufactured and marketed under several different trade names. Among them nylon 6 and nylon 66 are the two most manufactured polyamides. There are several other nylons such as nylon 46, nylon 610, nylon 612, nylon 10, and nylon 12 which are used for specialized applications.

In general, there are two types of nylons, i.e. nylon XY, and nylon Z. Nylon 66 and nylon 6 are the examples of these two types respectively. In nylon XY type, the X refers to the number of carbon atoms in the diamine monomer, whereas, Y represents the number of carbon atoms in diacid monomer. In nylon Z type, Z refers to the number of carbon atoms in the monomer.

2.2 Nylon 66

Nylon 66 type nylons are synthesized from a diacid and diamine. For nylon 66, hexamethylene diamine (H) and adipic acid (A) are reacted to form H-A salt. The salt is polymerized to produce nylon 66 in the following manner.



The purity of raw material is important in the polymer production and the specifications of these raw materials have been reported [1]. Hexamethylene diamine should be in the crystalline form with melting point of 40°C and boiling point of 204°–205°C. Adipic acid is in the white crystalline form with acid number of 368, with melting and boiling point of 152° and 216°C. The color, iron and water content are also controlled.

In the production process, the two monomers of nylon 66 are taken in the molar ratio of 1 : 1. These two components are reacted in methanol at elevated temperature, to obtain the salt which precipitates from methanol solution. The H-A salt is dissolved in water at concentration of 60%. The solution is heated to around 250°C for polycondensation for production of nylon 66. Loss of water in the process of polymerization should be taken into account for the net recovery of polymer [2]. Nylon 66 was earlier produced via a batch process with intermediate H-A salt. However, now the continuous process of production is favored for conversion of monomer to polymer.

To achieve desired molecular weights of the polymers, stabilization processes are used. This is achieved by taking slightly different than equivalent quantities of diacids and diamines. Say an excess of 1 percent of diacids is taken during the polymerization process, at a point of time, all long chain molecules will have carboxylic acid groups at both ends and polymerization does not proceed further. Thus an excess of one of the monomers decides the range of molecular weights achieved in the polymer. An equimolar ratio of 1 diamine to 1.015 diacid gives a polymer with a number average molecular weight of ~18000. This can also be achieved by adding say 1% of mono-functional reagent, such as acetic acid to equimolar quantities of diacids and diamines. Another method to make polyamides could be by using amino acids with one end as an amino group and another end as carboxylic acid. Typically, diamine and diacids are preferred for production of nylons as it is easier and cheaper to make these monomers compared to amino acids. There is no difficulty in making the monomers for making

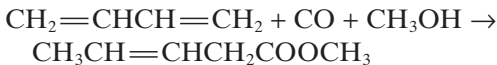
the typical polyamides and usually there are several different routes to select one, depending on the price and availability of raw materials.

2.2.1 Monomer synthesis for nylon 66

Adipic acid

The principal commercial processes are based on the oxidation of cyclohexane, which usually proceeds in two stages. The first step entails oxidation with air, yielding either a mixture of cyclohexanone and cyclohexanol or predominantly cyclohexanol. These reaction products are oxidized in second stage with nitric acid to adipic acid. This process employs a soluble cobalt oxidation catalyst, reaction temperatures in the range of 150°–160°C, pressures between 800 to 1000 kPa, and catalyst concentrations of 0.3–3 ppm.

An interesting approach involves a two-step carbonylation of butadiene. In the first step butadiene is reacted with carbon monoxide and methanol in the presence of dicobaltoctacarbonyl and heterocyclic structure containing a tertiary nitrogen moiety (pyridines, picolines, quinolines, isoquinoline):



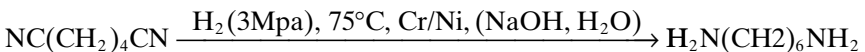
This reaction is carried out at 120°C and at pressure of 60 MPa. After removal of unreacted butadiene, the second step carbonylation is carried out at about 185°C and 3 MPa:



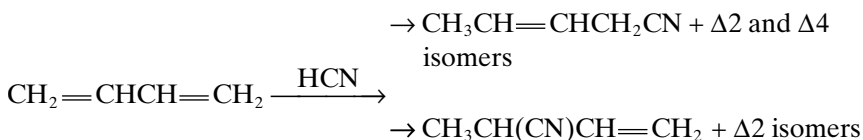
The dimethyl adipate is isolated by distillation and converted to adipic acid by hydrolysis.

Hexamethylene diamine

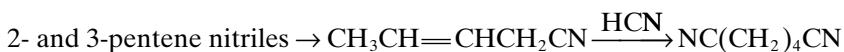
The commercial processes for manufacture of hexamethylene diamine entail hydrogenation of adiponitrile. It is a continuous liquid phase process that is usually conducted at 75°C and 3 MPa pressure in the presence of chromium containing Raney nickel catalyst and aqueous sodium hydroxide:



A newer DuPont process is characterized by the direct addition of HCN to butadiene. It is essentially a two stage process. The first step is a vapor phase operation. A gaseous mixture of butadiene, hydrogen cyanide, nitrogen, and hydrochloride in a ratio of 1:1:1:0.1 is contacted at about 215°C and atmospheric pressure with a copper magnesium chromite fixed bed catalyst for about 50 min:



The second step entails catalytic isomerization of the 2- and 3-pentene nitriles to 4-pentene nitrile, and the addition of a second mole of HCN:



2.3 Nylon 6

Nylon 6 is a nylon Z type of polymer, where the Z represents the number of carbon atoms in the monomer. Nylon 6 is typically produced from caprolactam in the following manner.



The purity of the caprolactam is critically assessed for the production of nylon 6 polymer. The specificities of the monomer are freezing point 69°C; permanganate number 71; molar ratio %; iron content as 0.5 ppm. Detailed analytical methods for purity analysis are reported in literature [3–5].

Caprolactam requires a catalyst, which converts small amounts of caprolactam to ϵ -aminocaproic acid which helps in polymerization process. The catalyst could be water, where the control of reaction is easy. Acid or base catalyst system may also be used, where the base catalyst system has the advantage of high production rate, high molecular weight, although the control of reaction in the system is rather critical. Some characteristics of catalyst system [6] are given in [Table 2.1](#).

2.3.1 Molecular weight in water catalyst system

In a water catalyst system the critical parameters during reaction are temperature of 225°–285°C, amount of water 5–10% and stabilizer content of 1% and time of polymerization.

Table 2.1 Influence of catalyst system on nylon 6 production

Parameter	Catalyst systems		
	Acid	Base	Water
Type	Strong, e.g. hydrochloric acid or their salts	Carbonate, hydride, alcoholate and hydroxide of alkali and alkaline earth metals	–
Rate	Fast	Very fast	Slow
Special condition	Anhydrous	Anhydrous	–
Yield	Low	High	High
Use	Not used commercially	Shows promise	Commercially used

The DP of Nylon 6 is governed by the following relationship

$$DP = (p + r + q)/(1 + r) (1 - p)$$

where

$$p = 1 - \{(X + Y)/(X_0 + Y_0)\}$$

$$q = X_{00}/X_0$$

and $r = Y_0/X_0$

Here X_0 and X represents the carboxyl group concentration at the start of polymerization and after some time, t , respectively. Y_0 and Y represent the amino group concentrations at the initial and final stage, respectively. X_{00} represents the initial concentration of carboxyl group of a monofunctional acid acting as a stabilizer. Acetic acid is typically used as a stabilizer.

2.3.2 Monomer synthesis for nylon 6

Caprolactam

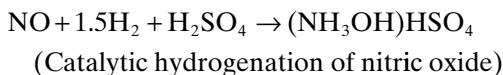
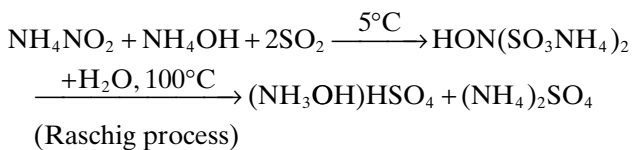
There are three important commercial processes for the caprolactam synthesis and all processes start from materials that belong to the group consisting of phenol, benzene, toluene, and cyclohexane. The principal intermediates are cyclohexanone and cyclohexanone oxime for process 1, cyclohexanone oxime for process 2, and cyclohexane carboxylic acid for process 3. The cyclohexanone may be produced by any of the following methods:

1. Catalytic hydrogenation of phenol and subsequent dehydrogenation of the resulting cyclohexanol.
2. One step catalytic hydrogenation of phenol using a palladium on carbon catalyst.
3. Catalytic oxidation (air) of cyclohexane to a cyclohexanol/cyclohexanone mixture.
4. Reductive catalytic hydrolysis of cyclohexylamine in one stage operation.

Though process 1 is still practiced, 2 and 3 are the most significant commercial processes. Cyclohexanone oxime may be produced by any of the following methods.

1. Reaction of cyclohexanone with hydroxylamine (process 1).
2. Photinitrosation of cyclohexane with nitrosyl chloride (PNC process) (process 2).

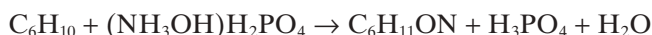
The hydroxylamine used for the reaction with cyclohexanone is obtained by the Raschig process or by catalytic hydrogenation of either nitric oxide or nitric acid.



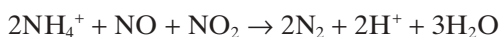
The catalytic hydrogenation of nitrate ions involves Pd/C as catalyst in a phosphoric acid ammonium hydrogen phosphate buffering system:



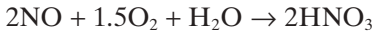
Since the hydroxyl ammonium ion is unstable, the reaction product is directly contacted with cyclohexanone in a toluene solution to effect formation of cyclohexanone oxime:



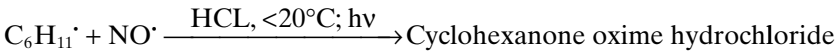
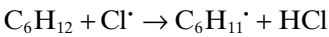
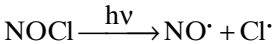
The aqueous H_3PO_4 - $\text{NH}_4\text{H}_2\text{PO}_4$ solution is reacted with a mixture of NO and NO_2 which results in the conversion of any ammonium ions to nitrogen:



Simultaneous introduction of air results in the formation of nitric acid which is recycled in the process.



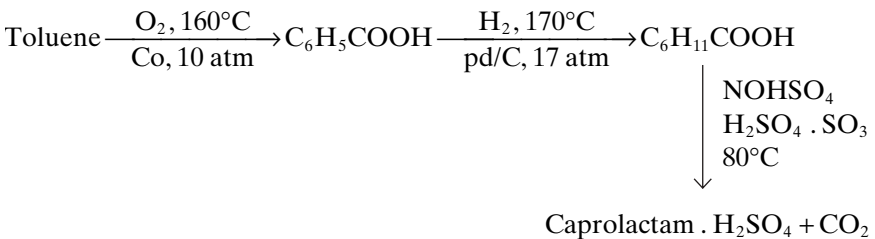
An interesting process developed and operated since 1962 by Toray for manufacturing cyclohexanone oxime is the photo-nitrosyl chlorination (PNC) process. This process may be explained by the following mechanism:



The nitrosyl chloride for synthesis is obtained by a sequence of reactions that includes:

1. Oxidation of ammonia: $2\text{NH}_3 + 3\text{O}_3 \rightarrow \text{NO}\cdot\text{NO}_2 + 3\text{H}_2\text{O}$
2. Formation of nitrosyl sulfuric acid: $2\text{H}_2\text{SO}_4 + \text{NO}\cdot\text{NO}_2 \rightarrow 2\text{NOHSO}_4 + \text{H}_2\text{O}$
3. Sulfuric acid regeneration: $\text{NOHSO}_4 + \text{HCl} \rightarrow \text{NOCl} + \text{H}_2\text{SO}_4$

Toluene is the starting material of a commercial process 3 developed by SNIA Viscosa. It involves the following reactions:



Reaction of cyclohexane carboxylic acid with nitrosylsulfuric acid in oleum results directly in the formation of caprolactam sulphate by a mechanism that entails simultaneous nitrosation, decarboxylation, and rearrangement of the formed oxime.

2.3.3 Molecular weights suitable for filament production

With appropriate molecular weights, it is possible to produce filaments through melt spinning process. Typically the number average molecular weight used for fiber production process is 18000–20000. Technical grade nylons are made from 24000–26000 number average molecular weight polymers. These high molecular weight nylons are produced by solid state

polymerization from low molecular weight chips obtained through melt polycondensation process [7].

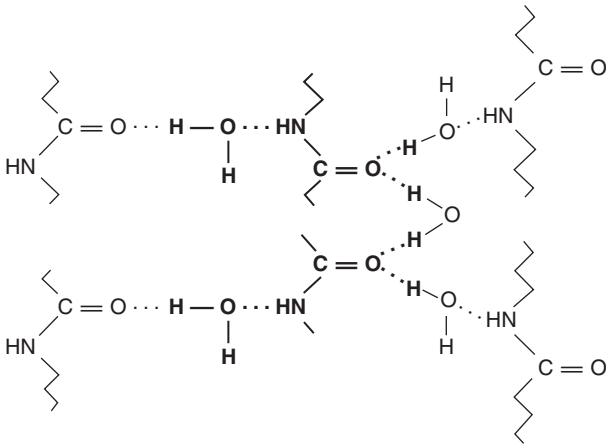
2.4 Thermal properties of nylon fibers

2.4.1 Glass transition temperature

Glass transition temperature (T_g) is associated with amorphous regions and has a significant effect on both processing and physical properties of nylon filaments. The segmental mobility during glass transition in nylon is associated with both flexibility of $-(CH_2)_n-$ sections, as well as to inter- and intra-molecular hydrogen bonding in the molecular chains. In nylon fibers, the most critical parameter for T_g is moisture regain, which is associated with flexibility introduced by water molecules acting as plasticizer. Amorphous nylon 6 has T_g varying from around -10°C in wet conditions to around 90°C in dry conditions. T_g also depends on number of (CH_2) units: as (CH_2) unit increases, T_g decreases [8]. In the semi-crystalline state of the filament, glass transition temperature is highly dependent on crystallinity, orientation as well as on moisture regain and the rates of testing. Typical T_g values for nylon filaments are in the range of 40°C to 55°C and increase to around 90°C in dry conditions. Dynamic mechanical methods give higher value of T_g by 20°C – 30°C , as compared to DSC method.

In the melt spinning process, essentially dry nylon is melted and spun in filament form. Filaments absorb moisture in the various steps of production process, i.e. during quenching, spin finish application and further processing. Thus, T_g dependence on varying moisture conditions during production processes is quite critical. T_g is known to have a non-linear relationship with moisture regain for amorphous nylons [9–12]. There have been several attempts to explain the T_g and moisture regain relationship [10, 13–15]; a reasonable explanation is obtained by three step moisture absorption [12] by nylons. The nature of absorption of molecules [16] is shown in Figure 2.1. In the process of moisture absorption from dry nylon, the initial water molecules form double hydrogen bonds between two carbonyl groups by means of free electron pairs on oxygen atoms and may be assessed as firmly bound. Water molecules are also attached by replacing the hydrogen bond between two carbonyl and amide groups and may be classified as loosely bound molecules. Further absorption can take place by multilayer formation of water molecules. These three different kinds of water molecules affect the T_g in a very different manner and this in turn affects the processing and properties of nylon fibers.

In the case of drawn nylons, some of the observations on T_g vs. regain are still valid. The results on linear expansion coefficients of Nylon 6 both parallel and perpendicular demonstrate this [17]. With increasing moisture

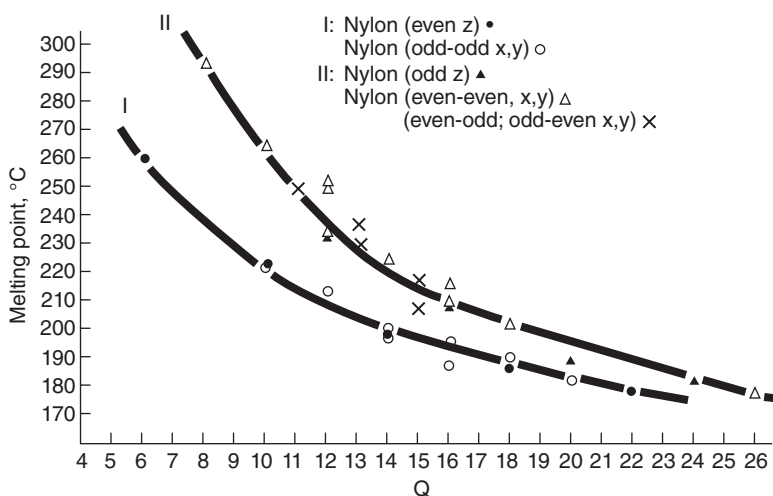


2.1 Interaction of amide groups with water in nylon.

regain from dry state, linear thermal expansion coefficient parallel to the fibre axis (α_{\parallel}) increases linearly. However, linear thermal expansion coefficient perpendicular to fibre axis (α_{\perp}) is negative up to 2% regain level, increases up to 4–5% of regain level and stabilizes thereafter. This particular variation of α_{\perp} can be explained in terms of varying intermolecular interactions between water and nylon molecule in the above regain range. The continuous increase in α_{\parallel} with regain level shows that there will be corresponding variations in properties.

Modulus of nylon fibre at low temperature has shown that initially, as regain increases from the dry state, modulus increases [18]. This implies that the initial water molecules are tightly bound and have a partial specific volume less than unity, thus making the state very rigid. Variation of torsional rigidity of nylon 6 fibers [19] is a function of regains and observes a maximum rate of change at 3% ratio regain. This corresponds to increased mobility [20] of loosely bound water molecules, as observed from NMR measurements at these regain levels. Stress ageing experiments on nylon 6 filaments indicate that stress induced microcrystal formation takes place during moisture absorption, in the regain range of about 2%.

Choice of moisture regain in the quenching zone in nylon filament production process is quite critical, as the moisture regain is changing rapidly. An RH level of 70% will be helpful, as the filaments will quickly attain the regain levels of ~3% in the highly dynamic filament formation process. Drawing process of nylon 6 is also carried out at around 55% RH corresponding to 3% regain levels. Choice of this level is related with minimum changes in T_g of the fiber with fluctuations in relative humidity in this range.



2.2 Melting point of aliphatic polyamides: Q (Nylon Z) = $2(z - 1)$, Q (Nylon x,y) = $x + (y - 2)$; (x,y,z - number of CH_2 groups per monomer unit).

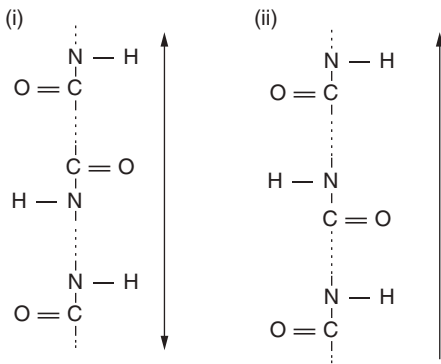
2.4.2 Melting temperature

Melting of nylon fibers is typical to semi-crystalline polymers, occurring in a range of temperatures. The melting range of nylon 6 is in the temperature range of $215^\circ\text{--}228^\circ\text{C}$, while the nylon 66 melting range is between 250° and 265°C . Melting of nylons is dependent on concentration of amide groups and number of CH_2 groups linking these groups. The variation of melting with number of CH_2 groups per monomer unit is shown in Figure 2.2 [21]. The figure further indicates that the melting also depends on symmetry of the structural units. Heat of fusion of α -crystal form for nylon 6 is 64 cal/g. , whereas nylon 66 has a value of 61 cal/g.

2.5 Physical structure of nylon fiber

2.5.1 Steric polarity in nylons

In general in polyamides, steric polarity results from invariable sequences of the CO and NH group [5]. Steric polarity is absent in polyamides of XY type, i.e. nylon 66, but is a distinct characteristic of Z type i.e. nylon 6. In the absence of directionality of XY type nylons, lattice disorders may be readily corrected by movement of chain along the chain direction. As shown in Figure 2.3 [22], steric polarity is absent in nylon 66 but is present in nylon 6. Stable polymorphic modifications i.e. α and γ crystals are possible in nylon 6 due to the directionality effect. Similarly, nylon 4 also has two highly distinguishable crystal forms, i.e. α and γ .



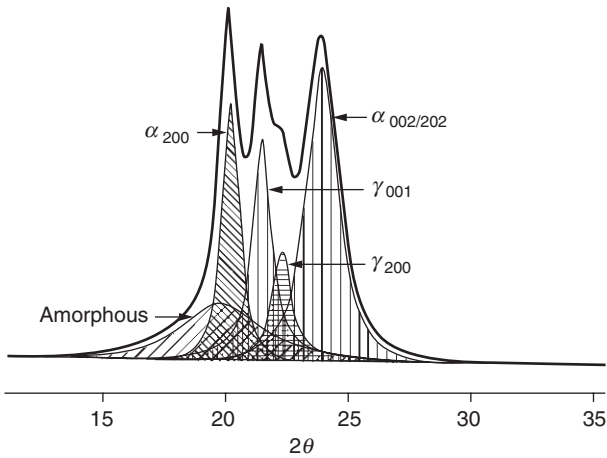
2.3 Steric polarity in (i) nylon 66 and (ii) nylon 6.

2.5.2 Semi-crystalline structure of nylon fibers

Nylon fibers are semi-crystalline in nature and the crystalline structure is significantly affected by the manner of hydrogen bonding between $-\text{CO}-$ and $-\text{NH}-$ molecules. Among the two crystal forms of nylon 6, α -crystal is characterized by anti-parallel extended chain arrangement in sheet like structure, with hydrogen bonds between adjacent chains. The stacking of these sheets is marked by an alternate up and down displacement of about 0.37 nm parallel to chain direction. The crystal form is monoclinic. The crystalline unit cell has eight repeat units [23].

Another crystal modification of nylon 6 is the γ crystal form. Adjacent chains in the γ form are aligned parallel to one another; however these chains are no longer fully extended but have a slight twist. The hydrogen bonding between adjacent chains is at 50° to the chain direction. In both crystal forms, hydrogen bonding is complete between amide and carbonyl groups. The strength of hydrogen bond in the α form is higher than the γ form. Due to differences in the two crystal forms, the density of the α form of 1.23 gm/cc is significantly higher than that of the γ form, having a value of 1.16 gm/cc. The γ form is stable only up to a temperature of around 170°C and gets converted to the more stable the α form at higher temperatures.

The filament production process is very sensitive to generation of different crystal forms. At low speed of spinning, the α -crystal form is dominant. At high speed of spinning, the γ -crystal form dominates (e.g. high speed spinning). Subsequent drawing process is easier with the γ form, being more deformable. The drawn and heat stabilized filaments have a dominant α -crystal form. Nylon 6, specifically as-spun filament-form contains a mixture of α , γ and pseudo-hexagonal forms. Rapid quenching of nylon 6 forms a molten state, resulting in bundle-like arrangement of chain segments of parallel and anti-parallel directionality, referred to as a



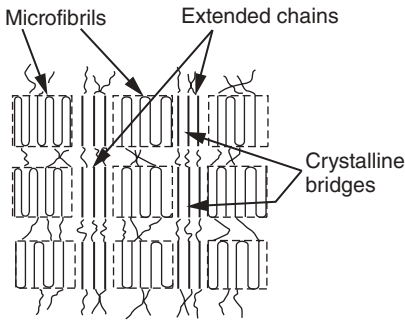
2.4 Experimental and fitted equatorial diffraction patterns.

pseudo-hexagonal form. This form is stable only up to 100–150°C and gets converted to the α or γ form depending on subsequent processing of spun filaments. However the α form, being more stable, dominates the stabilized filaments.

Figure 2.4 is a representative equatorial diffraction pattern of nylon 6 filaments [24]. The line analysis of diffraction pattern shows that the samples contain α and γ crystal forms along with amorphous regions. Such analysis can in general be used to obtain fractions of the crystal forms and crystallinity.

Nylon 66 has two very similar crystal forms i.e. α and β . The α -crystal form has an anti-parallel chain in sheet form, very similar to that of the α form in nylon 6. The stacking of hydrogen bonded sheets is characterized by a perpendicular distance of 0.36 nm and a displacement of successive sheets of about 0.5 nm in the chain direction. The α and β forms are differentiated by displacement of sheets in the chain direction being strictly in one direction for the α form and an alternate up and down for the β form. In the case of nylon 66, the α -form is slightly more stable than the β -form. Rapid cooled spun nylon 66 filaments also have a bundle-like arrangement of chains with pseudo-hexagonal arrangements, which get converted to stable crystal forms in subsequent processes of drawing and heat setting.

The actual crystal densities in a given fiber may be 1.19 gm/cc for the α -crystal form and 1.14–1.15 gm/cc for the γ -crystal form. The pseudo-hexagonal structure density is in the range of 1.13 gm/cc and a value of 1.09 gm/cc has been reported for amorphous phase.



2.5 Microstructure of highly drawn polyamide fibers.

Amorphous regions in fibers generally have an imposed orientation, in an otherwise random arrangement of molecular chains and designated as amorphous orientation. This could be thought of as chain extension being highest along the fiber axis. The actual amorphous density of the fibers is higher than 1.09 gm/cc, due to the presence of amorphous orientation.

2.5.3 Morphological structure

A reasonable morphological model for nylon fibers is described in terms of the three phase model with microfibrillar and inter-microfibrillar regions as shown in the Figure 2.5 [25]. It should be noted that a two phase model, consisting of crystalline and amorphous regions in fibers, does not adequately describe the fiber structure. The width of the microfibrils ranges between 60 and 200 Å. The microfibrils in turn consists of crystalline and amorphous regions in a series mode. Industrial grade filaments typically have crystalline and amorphous region lengths of ~60 Å and ~30 Å respectively. These crystalline and amorphous regions, arranged in a regular sequence along the fiber axis, act as a micro-lattice. In fact the regularity is sufficient to give diffraction maxima in the small-angle of x-ray scattering. Longitudinal dimensions of microfibrils are not well defined as is the case with this model type. Microfibrils are surrounded by inter-microfibrillar regions and consist of highly oriented molecular chains and are thus in some degree of pseudo-order [26–28]. Microfibrils in turn form an endless oriented network with branching and fusion more common than endings.

Existence of intra-fibrillar tie molecules has been proposed by Peterlin [29]. A comprehensive review of structural models has been recently published [30]. In the drawing process, nylons deform through micro fiber slippage forming a large number of interfibrillar tie molecules which appear

as a separate phase. Thus the modulus and strength of nylons are dominated by the amount of interfibrillar extended chains and should be considered as a separate phase.

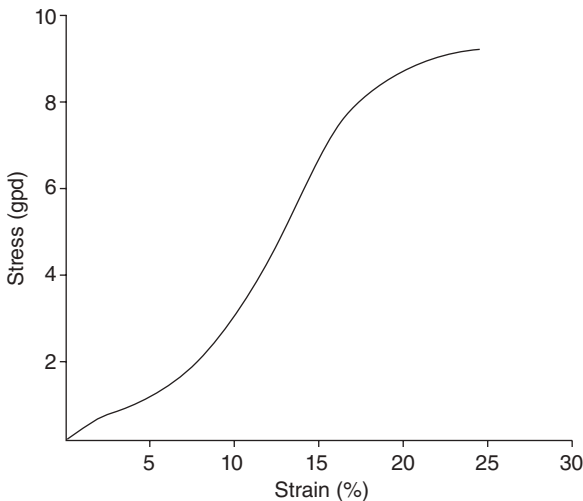
There is a significant interaction between microfibrils in nylons. The extended chains in interfibrillar regions are the strongest and have a profound effect on fiber strength. Thus strength can be increased by shearing off the surface of the microfibrils to make an interfibrillar domain. In the highly oriented state, microfibrils tend to fuse via epitaxial crystallization of extended chain molecules as shown in [Figure 2.5](#).

2.6 Mechanical behavior of nylon fibers

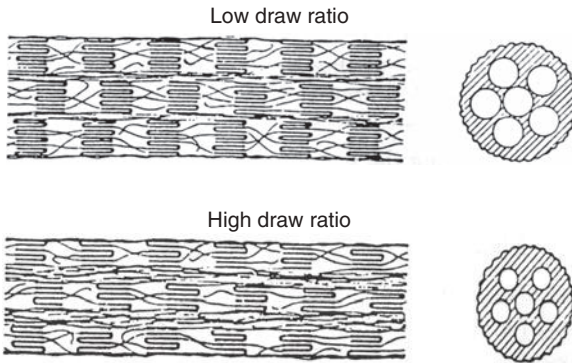
A typical stress-strain curve of nylon tire yarns is shown in [Figure 2.6](#). It is interesting to note that the initial modulus of the nylon is quite low. This is followed by a yield point and a sigmoid type of deformation as shown in the stress-strain curve. This behavior of nylons is unique and is related to combination of flexible $-(CH_2)-$ sections, occasional breakage of hydrogen bonds in amorphous regions and physical linking offered by the presence of crystalline regions. Further, nylons have large extensions to break combined with relatively high strength and thus result in high work of rupture.

2.6.1 Strength

The strength of nylon filaments can be assessed on the basis of the morphological models of these fibers as shown in [Figure 2.6](#). The inter micro-



2.6 Stress-strain curve of nylon yarn.



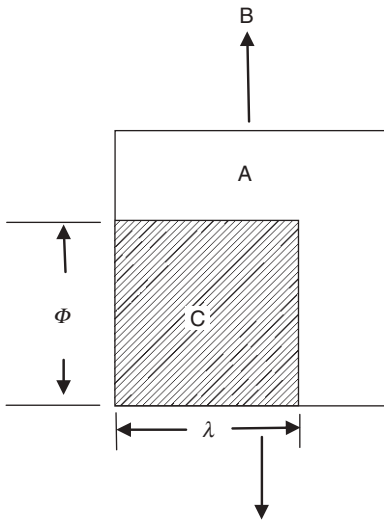
2.7 'Swiss cheese' fiber model.

fibrillar phase is the strongest element of the fiber. On the other hand the microfibril deformation is dominated by the presence of an amorphous region in series with the crystalline regions. On the other hand, the regular chain folding makes the microfibrils relatively weak with strength in the order of 2 gm/denier [31]. The amorphous domains are the weakest element and initiation of cracks is expected to start from them. In the case of highly drawn filaments, the microscopic crack [32] dimensions are similar to the microfibril diameter of $\sim 75 \text{ \AA}$. The number of amorphous domains per unit cross-sectional area is estimated to be $\sim 2.4 \times 10^{11} \text{ cm}^{-2}$. Taking the long period as 90 \AA , concentration of crack nucleation sites is around $2.6 \times 10^{17} \text{ cm}^{-3}$. This value is near to the concentration of free radicals found in the breakage of nylon 6 fiber.

One important conclusion from these observations is that the microcracks arising out of amorphous regions do not grow but become unstable and lead to catastrophic failure. Further, the failure is associated with minimum number of chain scissions. Morphological models [33] for low draw ratio and high draw ratio illustrate these facts as shown in Figure 2.7. Thus the strength depends on: (a) volume fraction of interfibrillar extended chain dimensions; (b) lateral dimension of microcracks; and (c) distance between the crystallites. The later factors reduce the stress at the tip of the microfibrils.

2.6.2 Modulus

Tensile and bending moduli are important properties of the fibers, affecting the final product properties. For a given fineness, bending modulus is proportional to the tensile modulus. Thus, the tensile modulus values are of significance and a lot of information is available. Crystal modulus values



2.8 Equivalent general mechanical model for representation of dynamic mechanical properties of two phase system.

(E_c) of select nylons are well-documented based on calculations using force constants associated with vibrational frequencies of the polymer chain. Contributions of crystal modulus depend on the load transfer between crystalline and amorphous regions in a two phase model of the fibers. An analysis of modulus can be done using Takayanagi's unit cube model [34] for these fibers as shown in Figure 2.8.

As there is orientation in amorphous regions, the moduli of these regions (E_a) depend on amorphous orientation function (f_a). The dependence of E_a on f_a has also been reported [34]. Modulus of the fibers based on unit cube model can be expressed as follows:

$$E_f = \lambda [(\phi/E_c) + (1 - \phi)/E_a] + (1 - \lambda) E_a$$

Table 2.2 gives the value of all the relevant parameters i.e. E_f , E_c , E_a , λ , ϕ for three different nylon 6 filaments having different draw ratios. For highly drawn samples, λ is much less than 1, which shows a dominant parallel response between crystalline and amorphous regions. Further λ , is approximately equal to ϕ , indicating a degree of isotropy in parallel and perpendicular directions. On the other hand the sample with the intermediate draw ratio, $\lambda \approx 1$ and $\phi \approx 0.57$. This corresponds to maximum anisotropy, i.e. coupling along the fiber axis is close to series response and in the perpendicular direction, it is a parallel response. Thus a simple two phase model approach for nylons gives satisfactory explanation for modulus values.

Table 2.2 The values of E_f , X_D , E_c , λ , Φ , $E\alpha$ for nylon filaments with draw ratios of X1.3 and X5.35

Draw ratio	$E_f, \times 10^{-10}$ dynes/cm ²	X_D	$E_c, \times 10^{-10}$ dynes/cm ²	λ	Φ	$E\alpha, \times 10^{-10}$ dynes/cm ²
1	2.35	0.63	12	0.80	0.787	0.70
3	4.80	0.56	25	0.98	0.570	2.34
5.35	5.50	0.34	25	0.52	0.654	3.26

2.6.3 Elastic recovery behavior

Nylon fibers have excellent elastic recovery behavior. This unique behavior relates to decrease in entropy on tensile deformation and recovery on stress removal, typical of time dependent rubber elastic effects. During deformation of nylons, the $-(CH_2)-$ sections in amorphous regions are typically mobile above the β -transition temperatures of $\sim -30^\circ\text{C}$ for nylons. However, regular restrictions are imposed in the mobile sections by hydrogen bonds. These mobile sections may be bigger in the absence of hydrogen bonds, but eventually get restricted as the chain enters the crystalline regions. A chance breaking of hydrogen bonds results in the creep behavior of nylons. On removal of load, the recovery process is due to entropic effects and occurs through breaking and reformation of hydrogen bonds. Typically crystallinity of the order of 50–70% in nylon filaments restricts the overall flow of molecular chains, and insures excellent recovery of nylons. It is worth mentioning that different nylons with varying hydrogen bond density have essentially the same recovery behavior. Interestingly, these observations hold for fairly large deformations of nylon filaments.

2.6.4 Relaxation behavior of nylon 6 and nylon 66 tire cord

Both nylon 6 and nylon 66 have been used in a range of applications interchangeably depending on local availability. For industrial grade applications, differences between nylon 6 and nylon 66 become apparent. Comparative relaxation behavior of these two classes of high tenacity nylon filaments is described, based on dynamic mechanical behavior and morphological parameters [34]. $\tan \delta$ peak for nylon 66 is at $\sim 99^\circ\text{C}$ and for nylon 6 it is at 88°C . Due to lower T_g , the heat generation builds up faster from room temperature for nylon 6 than that for nylon 66. Nylon 6 also has higher loss peak height than that of nylon 66, whereas nylon 66 has broader loss peak than nylon 6. Nylon 6 also has slightly lower crystallinity than

Table 2.3 Comparison of morphological factors for highly drawn nylon 6 and nylon 66 filaments

	Degree of crystallinity, %	Amorphous orientation	Long period Å	Size of amorphous domain, Å
Nylon 6	67	30	86	28.7
Nylon 66	70	36	91	30.3

that of nylon 66. The higher loss peak along with other factors indicates greater heat generation for nylon 6. Nylon 66 has higher thermal stability due to higher melting temperature as compared to nylon 6. These factors combine together to make nylon 66 filaments superior in demanding industrial applications. For these reasons, applications such as airplane tires are made entirely from nylon 66 cords. These observations are supported by morphology data as given in Table 2.3 and these differences relate to crystallinity, integral breadth in amorphous orientation, long period and size of amorphous domains.

2.6.5 Compressive stresses due to twisted structure

Generally twisted structures are used as nylon tire cords as well as other industrial applications. Twisted structures have large compressive stresses and on tensile deformation, these stresses increase significantly. It is likely that deformation reaches the non-linear limit, as this limit is rather low in compression. On tensile loading of the twisted structure, there is further increase in compressive stresses and thus further decay in properties. For these reasons rope structures with a core of parallel threads and a sheath of braided structures is preferred over a twisted structure for industrial applications using large loads.

2.7 Applications of nylon fibers

Due to good elastic recovery, low initial modulus, excellent abrasion resistance and high resistance to rupture, nylon has been used in a very large number of applications. Nylon fibers are used in both apparel and industrial sectors. Light weight and sheer garments are produced from nylon 6 and nylon 66, where low modulus, high strength and good abrasion resistance are of particular importance. Fabrics made from 15 denier monofilaments are used as ladies' stockings. They show excellent shape retention due to the elastic recovery behavior of nylons. Setting in steam allows

dimensional stability, permanent pleating while liveliness is also reduced. These fabrics may not require ironing. Socks are mostly made from nylon due to similar reasons. Fabrics made from fine filament are extensively used for sarees. Furs from nylon are also popular due to recovery behavior and long life. Wool is blended with nylon to improve its durability.

In technical textiles, nylon fibers are widely used for a number of applications. Nylon is amongst the best carpet fibers because of resilience and excellent aberration resistance and is very useful under heavy traffic. Nylon bulk continuous filament is used for this purpose. Safety belts in cars, hoses, typewriter ribbons, and light weight canvas for luggage are exclusive domains for nylon filaments. Polyurethane coated nylon fabrics are used for making hot air balloons.

Multifilament nylon yarns find extensive applications for reinforcing rubbers such as tires, with the filament denier ranging from 840 to 1620. These are twisted as multi-strand cord, which improves flex fatigue and with high surface areas for easier bonding with latex. In fact most tires for trucks and airplanes are made from nylon tire cords. Nylon ropes and cordages have strength, durability, and resistance to water. Fishing nets are mostly made from nylon twine due to excellent elastic recovery and high wet strength. Sail cloth made from nylon allows deformation due to wind and recovery on reduction of wind speed, and thus allows optimum advantage of the wind speed.

Strimmer lines used for cutting grass are dominantly made from nylon 6, nylon 66, and nylon 69 monofilaments [35]. These filaments provide the correct balance of flexibility, abrasion resistance and thermal dimensional stability. There is a rapid change in local temperature of these lines and stabilized nylon restricts fusing. A very high diameter uniformity and low shrinkage are required for these filaments. Nylon monofilament of 1.5 mm diameter is used for garden strimmer lines and a diameter between 2.0 to 3.0 mm for agricultural cutters.

Monofilament of polyester and nylon are woven to make conveyor belts for manufacture of paper. The fabric is open mesh with good dimensional stability having a wide width of up to 10 m. Typical dimensions of monofilaments used are in the range of 0.15–0.30 mm. Nylon filaments are in the underside of the conveyor in a nylon/polyester combination to improve wear resistance against the machine frame. Further, nylon filaments do not split longitudinally under compression from machine components. Using small groups of twisted monofilaments also further dissipates the compressive forces and a resilient bare weave is achieved. Umbrella cloth is made from nylon due to diameter swelling behavior. Ribbons for printers, bolting cloths, sutures and toothbrush bristles are further applications of the nylons worth mentioning.

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