Microbial 1,3-Propanediol, Its Copolymerization with Terephthalate, and Applications

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Contents

Abstract Poly(trimethylene terephthalate) (PTT) fibers, as a new type of polyester, are characterized by much better resilience and stress/recovery properties than poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). PPT chains are much more angularly structured than PET and PBT chains and such chains can be stretched by up to 15% with a reversible recovery (Ward et al. 1976). These properties make PTT highly suitable for uses in fiber, carpet, textile, film, and engineering thermoplastics applications. 1,3-Propanediol (PDO), as one of the polyester raw materials for PTT, has also attracted interest.

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In the 1990s three technical processes for the production of PDO were developed. The first process used acrolein, and was developed by Degussa-Hüls; this technology was sold to DuPont in 1997. The second was developed by Shell with ethylene oxide as the substrate. These two processes are all classic chemical processes. Recently, the biological process of PDO production with glycerol or glucose as raw materials in one or two steps has been considered as a competitor to the traditional petrochemical routes. It has advantages such as mild reaction conditions, good selectivity of product, environmental friendliness, and use of a renewable feedstock. With the development of biotechnology, especially gene manipulation technology, microbial PDO has prospects for the production of PTT.

1 Introduction to 1,3-Propanediol

1,3-Propanediol, well known as PDO, is an organic compound with the formula $HOCH_2CH_2CH_2OH$. Usually PDO is colorless, has a slightly sweet taste, and is a viscous liquid which is easily miscible with water and ethanol. More details on the physical properties of PDO are shown in Table 1.

PDO has been known by for more than 100 years, and has been applied widely in many industrial applications, such as composites, adhesives, laminates, coatings, moldings, aliphatic polyesters, and antifreeze. From the 1990s, more and more efforts were paid to the preparation of PDO on a large scale because of its attractive potential application in the synthesis of fibers of poly(trimethylene terephthalate) (PTT), which is thought of as another promising compound compared with its similar counterparts poly(ethylene terephthalate) (PET) from the 1950s and poly(butylene terephthalate) (PBT) from the 1970s. PTT was considered as one of six new chemicals in 1998 in the USA.

2 PDO Production by Chemical Methods

All the chemical processes for the preparation of PDO have a similar intermediate, 3-hydroxypropionaldehyde, which is chemically synthesized using different chemical catalysts with a variety of feedstocks, and then is reduced to PDO using hydrogen

Table 1 Properties of 1-3-propanediol (Daubert and Danner 1989)

Properties	Values	Properties	Value
Molecular mass	76.10 Da	Viscosity	52 cP (20°C)
Boiling point	214.4°C (101.3 kPa)	Density	1.0526 g/cm (20°C)
	103.0°C (1.33 kPa)	Flash point	ASTM D-92 79°C
Melting point	−26.7°C	Rate of evaporation	0.016 (nBuOAc =1)
Refractive index	1.4386 (25°C)	Surface tension coefficient	46.2 mN/m

under chemical catalysis. This step is usually easy compared with the preparation of 3-hydroxypropionaldehyde. Two processes which have industrial applications have been developed by Degussa using propylene and Shell using ethylene oxide, respectively. Some other methods have also been reported.

2.1 Degussa Process Using Propylene as a Feedstock

This process consists of a three-step reaction: propylene is oxidized to acrolein, acrolein is hydrated to 3-hydroxypropionaldehyde, which then is reduced to PDO (Arntz 1991).

1. Oxidation of propylene to acrolein

$$CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CHCHO$$

2. Selective hydration to 3-hydroxypropionaldehyde

$$CH_2{=}CHCHO + H_2O \rightarrow HOCH_2CH_2CHO$$

3. Catalytic hydrogenation to PDO

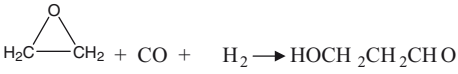
$$HOCH_2CH_2CH_2OH + H_2 \rightarrow HOCH_3CH_2CH_2OH$$

The key step in this process is the hydratation of acrolein, where various by-products are generated, and the quality of PDO is dependent on the hydroxylation of acrolein. So a high-performance catalyst which can selectively hydrate acrolein to form 3-hydroxypropionaldehyde is important for the industrial application of this process. Meanwhile, the instability and toxicity of acrolein are negative factors in this process (Fig. 1).

2.2 Preparation of PDO Using Ethylene Oxide as a Feedstock

This route consists of a two-step reaction. Firstly, ethylene oxide is carbonylated with carbon monoxide and hydrogen to form 3-hydroxypropionaldehyde. 3-Hydroxypropionaldehyde is purified and then reduced to PDO by hydrogen. The chemical catalysts used in the route are important for the selectivity and yield of the products, especially in the first reaction. The availability on a large scale with low cost and stability of ethylene oxide merits the use of this route, but the high cost of equipment and difficulty in preparing the catalysts hamper its industrial applications (Slaugh et al. 1995, 2001).

(1) Hydroformylation of ethylene oxide to 3-HPA



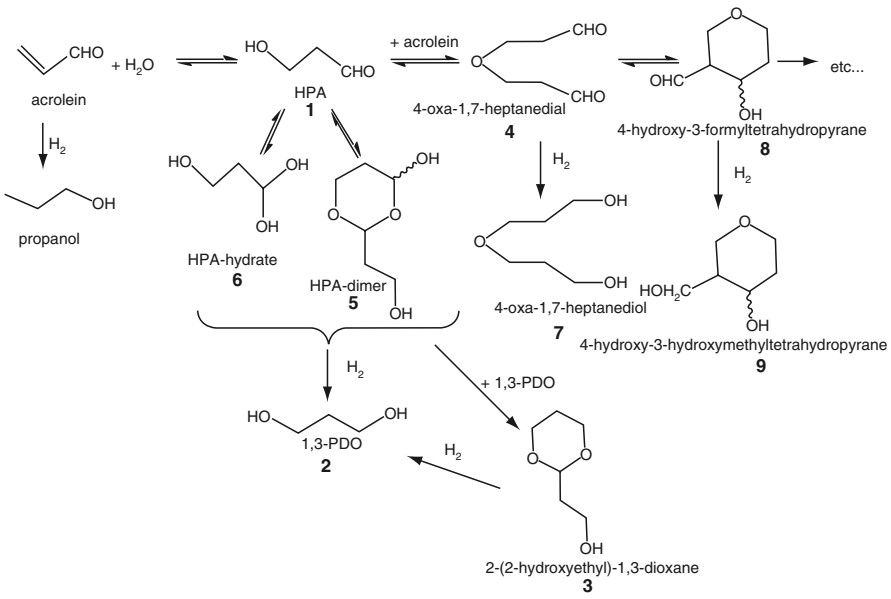


Fig. 1 Reactions involved in the process of the preparation of 1,3-propanediol (PDO) from propylene

(2) Catalytic hydrogenation to PDO

$$HOCH_2CH_2CHO + H_2 \rightarrow HOCH_2CH_2CH_2OH$$

2.3 Preparation of PDO via Selective Dehydroxylation of Glycerol

PDO can also be prepared by reductive dehydroxylation of the second carbon of glycerol, which includes three steps: acetalization, tosylation, and detosyloxylation. Firstly, glycerol is acetalized with benzaldehyde, a preferred hydroxyl group protection reagent, to protect the first and third hydroxyl groups of glycerol. Then the second conversion is the tosylation of acetalized glycerol at the first and third hydroxyl groups into 5-hydroxy-2-phenyl-1,3-dioxane, to transform the hydroxyl group into an easy-leaving state (a tosyloxyl group in this case). The final step of the conversion is a detosyloxylation reaction followed by a hydrolysis reaction to remove the tosylated hydroxyl group of glycerol and release the protecting reagent (Fig. 2) (Wang et al. 2003).

One problem with this process is the by-product generated in the first step, which will lower the yield of desired compounds and add to the difficulty of operations.

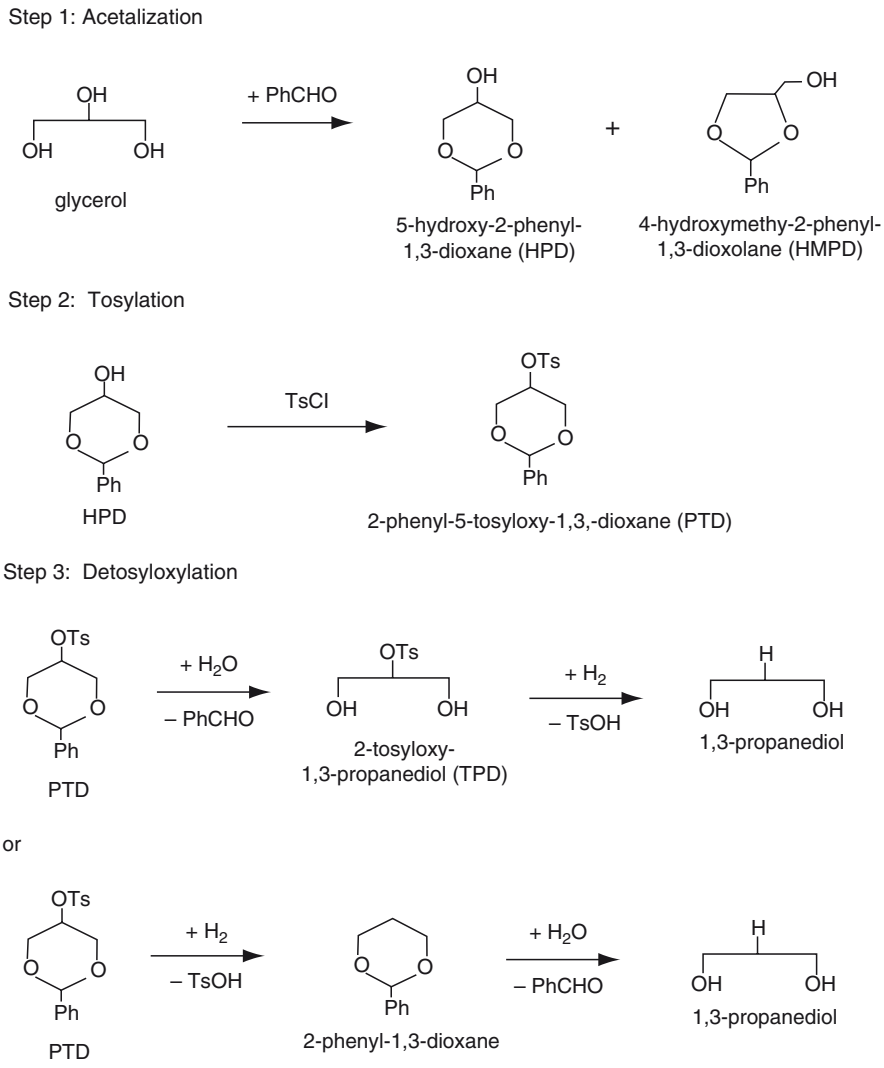


Fig. 2 Reactions involved in the selective dehydroxylation of glycerol to PDO

2.4 Other Processes Reported for the Preparation of PDO

Formaldehyde and acetaldehyde easily undergo aldol-condensation reactions to form 3-hydroxypropionaldehyde using KOH as a catalyst, and then aluminum isopropoxide catalyzes the reduction of 3-hydroxypropionaldehyde to PDO after removal of KOH via an ion-exchange resin. This route was firstly reported in a patent from India. The formaldehyde and acetaldehyde feedstocks used in this method

are cheap and are available on a large scale. But the yield and selectivity of the condensation reaction of formaldehyde and acetaldehyde need to be proved, and the cost of the catalyst is another factor that needs to be taken into account (Malshe 1999).

3 PDO Production by Microbial Fermentation

Today a bioprocess for the preparation of an industrial chemical is an attractive option compared with a traditional chemical process. The same is valid for preparation of PDO, and the biosynthesis process is attracting more and more attention because of the relatively low cost, mild reaction conditions, and environmental friendliness.

3.1 Microorganisms and the Metabolic Pathway

As early as the nineteenth century, it was found that microorganisms can generate PDO by metabolizing glycerol. Only a narrow range of microorganisms are able to produce PDO by fermenting glycerol, including *Klebsiella pneumoniae*, *Enterobacter agglomerans*, *Citrobacter freundii*, *Clostridium acetobutylicum*, *Clostridium butyricum, Clostridium pasteurianum*, *Lactobacillus brevis*, and *Lactobacillus buchneri* (Zeng et al. 1994; Barbirato et al. 1995; Schutz and Radler 1984; Boenigk et al. 1993; Biebl and Marten 1995; Forsberg 1987). These bacteria belong to different families and genera (Fig. 3).Among them, more attention has been paid to *K. pneumoniae, C. freundii*, and *C. butyricum* because of their higher PDO yield and productivity in PDO production. In addition, *Aspergillus niger* and *Aspergillus oryzae* have also been reported to be able to produce PDO from glycerol, but a very low production capacity was obtained (Yuan et al. 2006)

The production of PDO from glycerol is generally performed under anaerobic conditions in the absence of other exogenous reducing equivalent acceptors (Laffend et al. 1997). The PDO pathway is a dismutation process (Fig. 4). Through the oxidative pathway, glycerol is dehydrogenated by an NAD^+-linked glycerol dehydrogenase to dihydroxyacetone, which is then phosphorylated by PEP- and ATP-dependent dihydroxyacetone kinases. Through the parallel reductive pathway, glycerol is dehydrated by the coenzyme B_{12} dependent glycerol dehydratase to form 3-hydroxypropionaldehyde. 3-Hydroxypropionaldehyde is then reduced to the major fermentation product PDO by the $NADH_2$-linked PDO dehydrogenase, thereby regenerating NAD^+ (Fig. 3).

The PDO production is regulated by the *glp* regulon and the *dha* regulon (Zeng and Bieb 2002). The gene expression in the *dha* regulon can be induced by dihydroxyacetone (Forage and Lin 1982). The genes coding for the enzymes of glycerol metabolism, i.e., glycerol dehydratase (*dhaB*, *dhaC*, *dhaE*), PDO oxidoreductase (*dhaT*), glycerol dehydrogenase (*dhaD*), dihydroxyacetone kinase (*dhaK*), and a

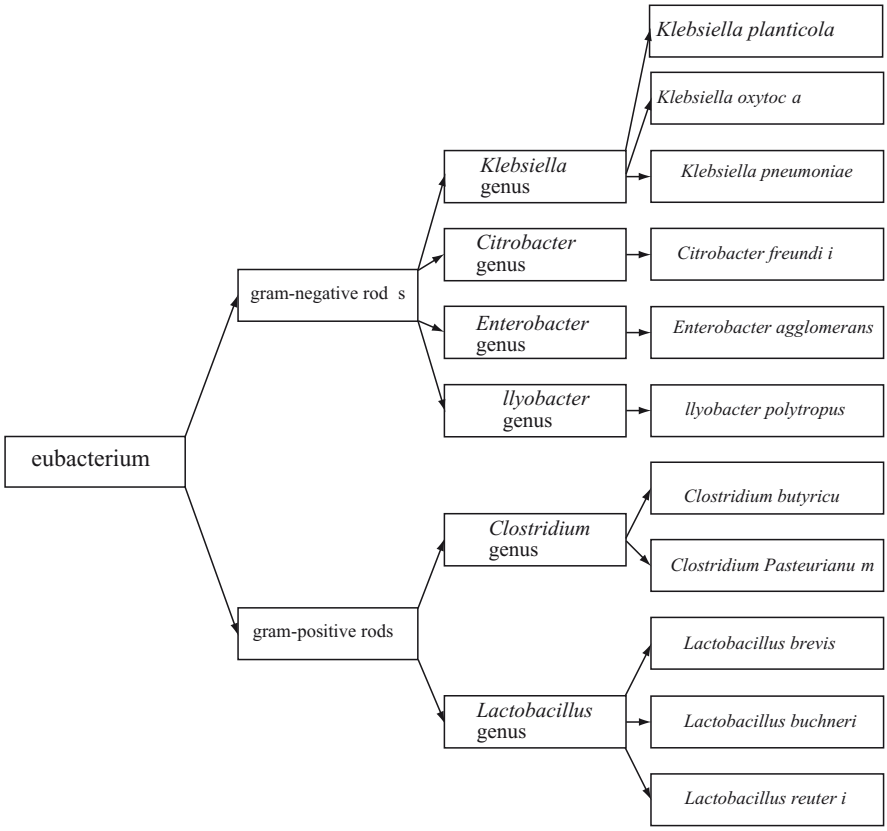


Fig. 3 The classification chart of wild-type bacteria reported in PDO production

putative regulatory gene (*dhaR*), have been cloned and sequenced (Fig. 5) (Sprenger et al. 1989; Tong et al. 1991; Tobimatsu et al. 1996; Daniel and Gottschalk 1992; Seyfried et al. 1996).

It has also been reported that, in the presence of oxygen, glycerol is metabolized through a completely different pathway regulated by the *glp* regulon. The glycerol is first converted to glycerol 3-phosphate under the catalysis of glycerol kinase, and then glycerol 3-phosphate is oxidized to dihydroxyacetone phosphate by a dehydrogenase. The *glp* regulon is constituted from six genes, including *glpFK* (membrane protein and glycerokinase), *glpTQ* (glycerophosphodiester phosphodiesterase), *glpABC* (anaerobic *sn*-glycerol 3-phosphate dehydrogenase, and *glpD* (*sn*-glycerol 3-phosphate dehydrogenase). The regulator gene *glpR* is near to *glpD*, which encodes an inhibitor of 33 kDa. The genes *glpE* and *glpG* are located between *glpD* and *glpR*; however, the function of the former two genes is not clear (Forage and Lin 1982; Koch et al. 1964; Ruch and Lin 1975).

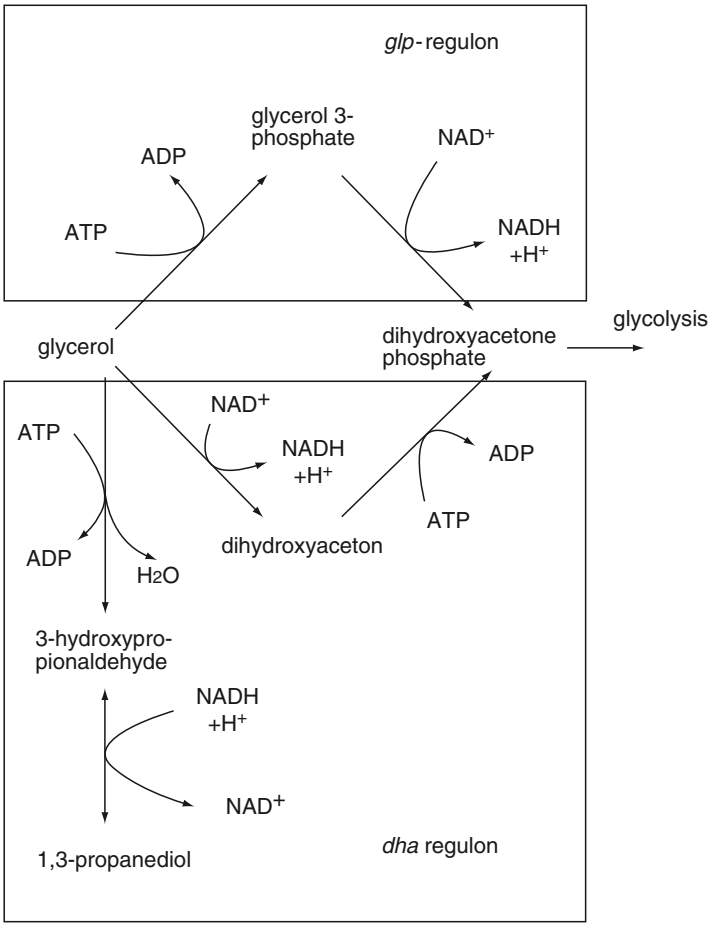


Fig. 4 Glycerol metabolic pathway in *Klebsiella pneumoniae*

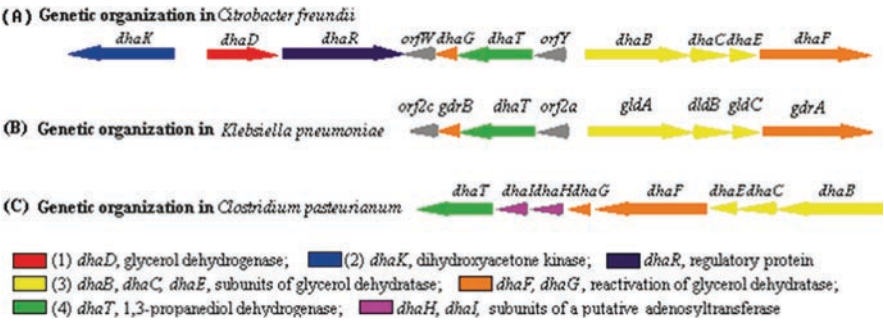


Fig. 5 Structure and function of genes in the *dha* regulon

In addition to these native PDO producers, recombinant organisms have also been constructed to enhance PDO production with the development of recombinant DNA technology. The main effective methods for genetic modification are decribed next.

3.1.1 Gene Overexpression of Key Enzymes

Glycerol dehydratase, as an example of a key enzyme, was demonstrated to be a rate-limiting enzyme (Abbad Andaloussi et al. 1996; Ahrens et al. 1998) in the PDO biosynthesis pathway, and is encoded by the three structural genes *gldA*, *gldB*, and *gldC* in the case of *K. pneumoniae* (Tobimatsu et al. 1996) and *dhaB*, *dhaC*, and *dhaE* in the case of *C. freundii* (Seyfried et al. 1996). Overexpression of the glycerol dehydratase gene is expected to enhance PDO production.

3.1.2 Knocking Out Genes Responsible for the Formation of Undesired By-Products

During the production of PDO, the synthesis of by-products such as acetic acid, lactic acid, and ethanol will decrease the yield of PDO. On the other hand, a high concentration of accumulated by-product, such as lactic acid, will also lead to difficulties in extracting PDO. So, blocking the synthesis of the by-products would be a good way to increase the PDO yield.

3.1.3 Strain Construction To Produce PDO from Glucose Directly

Lots of work has been done to construct a strain to utilize glucose because glucose as a substrate is much cheaper than glycerol in PDO production. However, there is no microbial wild-type strain has been found capable of converting glucose directly to PDO by now.

The conversion of glucose to PDO requires the combination of two natural pathways: glucose to glycerol and glycerol to PDO. The best natural pathways for the production of glycerol are found in yeast. *Saccharomyces cerevisiae* produces glycerol from the glycolytic intermediate dihydroxyacetone 3-phosphate using two enzymes: dihydroxyacetone 3-phosphate dehydrogenase and glycerol 3-phosphate phosphatase. The natural pathway for the production of PDO from glycerol requires two enzymes: glycerol dehydratase and PDO dehydrogenase. To construct a single organism to produce PDO from glucose, one could insert the glycerol pathway into a natural PDO producer, or the PDO pathway into a natural glycerol producer. Although both of these approaches seem simple and direct, there are problems involving natural regulation of the pathways. The third way is to build both pathways into a host that could do neither step (Fig. 6). DuPont has successfully constructed strain of *Escherichia coli* containing the genes from *S. cerevisiae* for glycerol production and the genes from *K. pneumoniae* for PDO

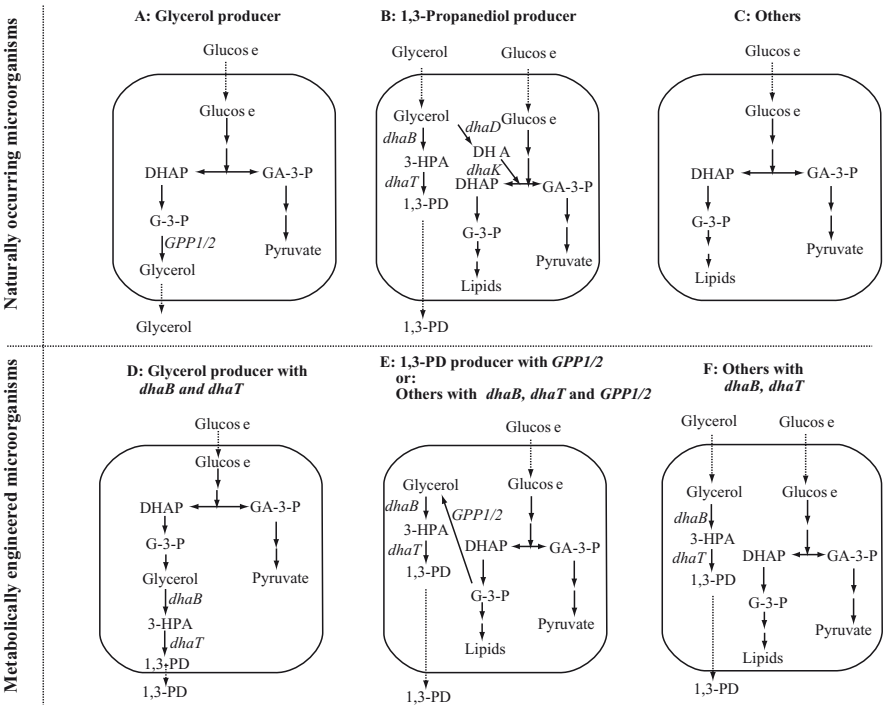


Fig. 6 Construction of recombinant microorganisms producing PDO from glucose (Biebl et al. 1999)

production. The final concentration of PDO produced by engineering *E. coli* reached 135 g/L (Nakamura and Whited 2003) using glucose as a feedstock. *E. coli* provides several advantages of other systems. *E. coli* is closely related to *K. pneumoniae* and *C. freundii*, but it does not naturally produce glycerol or PDO, and there is no natural regulation to overcome. *E. coli* is the most completely studied organism and its metabolism and physiological characteristics are well characterized. A large number of metabolic mutants have been constructed and analyzed. In addition, *E. coli* has been used in large-scale fermentations and production on an industrial level.

3.2 Fermentation Technology

PDO can be produced by microorganisms by fermentation and some by-products were obtained, such as lactic acid and 2,3-butanediol. The metabolite pathway of glycerol fermentation under anaerobic conditions and the fermentation product are described in Fig. 7.

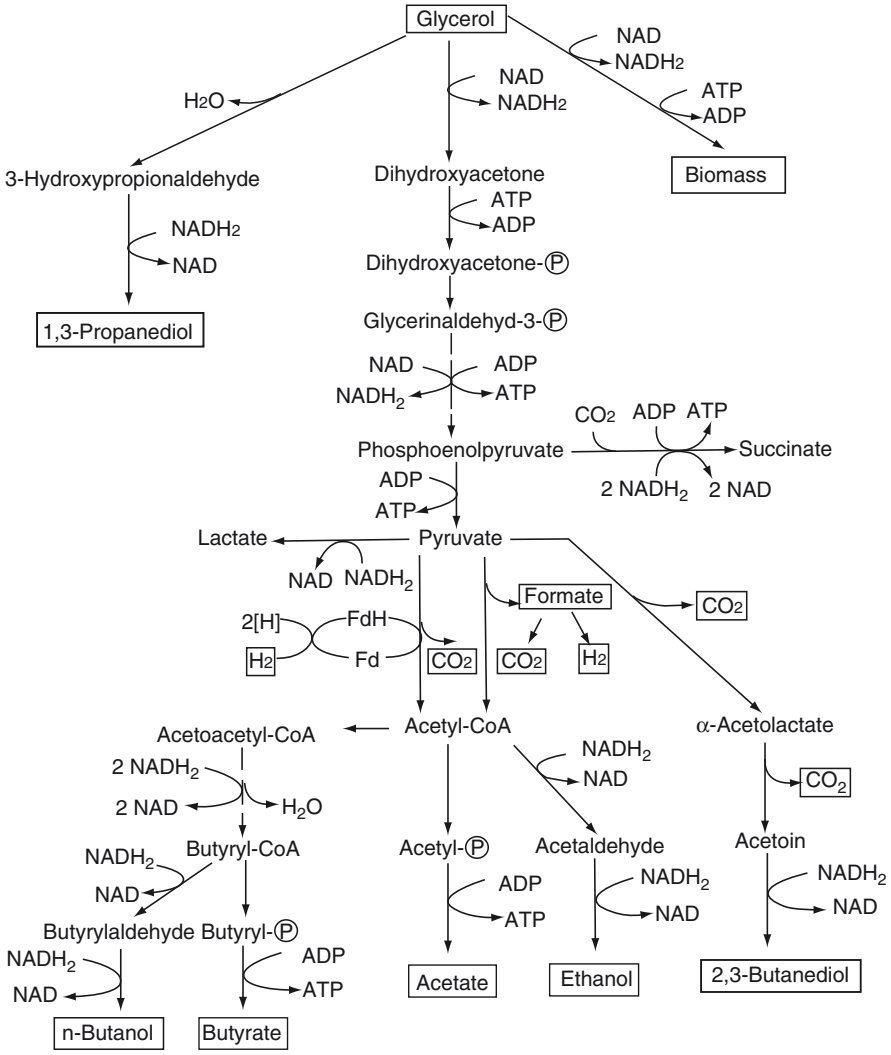


Fig. 7 Biochemical pathways of glycerol fermentation under anaerobic condition

Generally, the maximum concentration of PDO was obtained in batch and fed-batch cultures. Continuous culture has the advantage of relatively high productivities, but the PDO concentration was lower than that of batch fermentation. Günzel et al. (1991) studied the batch fermentation of PDO by *C. butyricum* DSM in a 2-L whisk and a 1.2-L airlift fermenter; the PDO concentration was 50–58 g/L. Cameron et al. (1998) studied the fed-batch fermentation in a 5-L fermenter with *K. pneumoniae* ATCC 25995; a PDO concentration and productivity of 73.3 g/L and 2.3–2.9 g/(Lh) were obtained. Menzel et al. (1997) studied the continuous fermentation of

glycerol by *K. pneumoniae* DSM 2026 in a 2-L fermenter; a higher productivity of 4.9–8.8 g/(Lh) was obtained, but the PDO concentration was just 35.2–48.5 g/L.

To enhance the PDO production and decrease the production cost, some new technology has been developed in the past few decades.

3.2.1 Micro-Aerobic Fermentation of PDO

The conventional PDO fermentation was performed under anaerobic conditions. However, recently, many investigations have focused on optimizing the fermentation conditions as well as exploring the metabolic mechanism in *K. pneumoniae* under micro-aerobic or mild aerobic conditions (Wang et al. 2001; Huang et al. 2002; Chen et al. 2003). In comparison with anaerobic cultivations, microbial production of PDO under micro-aerobic conditions has attracted much attention owing to low equipment investment and power consumption on an industrial scale. Under aerobic conditions, the conversion is mainly catalyzed by the *glp* system (Forage and Lin 1982). Cheng et al. (2004) compared different aeration strategies in the fed-batch fermentation of PDO by *Klebsiella oxytoca*; a PDO concentration of 69.6 g/L was obtained in a 5-L fermenter with an anaerobic–aerobic two-stage strategy. Liu et al. (2007) studied the PDO fermentation from glycerol by *K. pneumoniae* under micro-aerobic conditions and the final PDO concentration, molar yield, and volumetric productivity were 72 g/L, 57%, and 2.1 g/(L h), respectively. In the study of Zheng et al. (2008), the PDO concentration reached 74.07 g/L, and a high PDO yield and productivity of 0.62 mol/mol and 3.08 g/(L h), respectively, were obtained using *K. pneumoniae* under aerobic conditions.

3.2.2 PDO Production Using Glucose as an Auxiliary Substrate

Glucose, as a cheap carbon source, is often used as a hydrogen-donor substrate instead of the fraction of glycerol to provide both reducing equivalents for PDO formation and ATP for biomass. A higher yield of PDO to glycerol was obtained by using glucose as a cosubstrate. Abbad Andaloussi et al. (1995) studied the variation of carbon atoms and electronic flow of the PDO continuous fermentation of *C. butyricum* DSM 5431 by using glucose as the auxiliary substrate; the PDO yield increased from 57 to 92% compared with when glycerol was used as a substrate. In the study of Biebl and Marten (1995), a high concentration of glucose in the culture medium appeared to strongly inhibited the glycerol dehydrogenase and PDO dehydrogenase activities involved in the production of PDO (Malaoui and Marczak 2001).

3.2.3 PDO Production by Crude Glycerol

To enhance the yield of PDO and decrease the cost of production, strategies involving the utilization of raw materials by cells capable of resisting the impurities in the medium have been utilized (Papanikolaou et al. 2000; Barbirato et al. 1998) Raw,

unpurified glycerol, which does not need further purification, has been used in this type of fermentation. For example, a large quantity of low-cost by-product crude glycerol is produced in biodiesel production. Conversion of glycerol into higher value-added products such as PDO can decrease the production cost and it is an important process to integrate with biodiesel production. Tsinghua University studied the PDO fermentation by the genetically modified strain HR526 with the by-product glycerol of biodiesel; the PDO concentration reached 106 g/L. In 2008, the demonstration was finished in the pilot plant and a facility with capacity of 4,000 ton/year PDO is running at Hunan Rivers Bioengineering Company, China (Xu et al. 2009).

3.2.4 Using Glucose as the Substrate To Produce PDO

There has been growing interest in a more economical route that utilizes glucose as a lower-cost feedstock. The process was realized either by two-stage fermentation and mixed culture, or by recombinant microorganisms, because there is no natural microorganism that can directly convert glucose into PDO by now. Haynie and Wagner (1996) studied the mixed culture of yeast producing glycerol and bacteria producing PDO by using glucose as a substrate, but because of the different culture conditions and the formation of PDO as a result of glucose concentration inhibition, the mixed culture is not the best option. The two-stage fermentation technology has been studied to convert glucose into PDO. The first step is to use recombinant *E. coli* or yeast to convert glucose into glycerol; the second step is to convert the glycerol converted in the first step to PDO (Huang et al. 2002). Also, as mentioned already, DuPont developed a metabolically engineered organism that could produce PDO at a rate of 3.5 g/(L h), with concentration of 135 g/L and a yield of 0.62 mol PDO/mol glucose.

3.3 Separation and Extraction

PDO produced via fermentation contains residual organic impurities such as water, glucose, organic acids, salts, glycerol, and other compounds. Isolation and purification of PDO from a fermentation source therefore has significant and unmet challenges. Given the high boiling point and hydrophilicity of PDO, economic separation of PDO from those contaminants is difficult. The downstream processing of biologically produced PDO usually includes three main steps as shown in Fig. 8.

The first step is the separation of microbial cells, mostly by using membrane filtration or high-speed centrifugation, including pretreatment such as adjusting the pH with a base or adding a flocculant (e.g., chitose or synthetic cationic flocculants based on polyacryamide) into the broth. Flocculation precipitation on an industrial scale attracts attention owing to its simplicity if cheap and effective flocculants are available. Chitosan and polyacrylamide have been tested for this purpose. By combined use of chitosan and polyacrylamide at optimal concentrations of 150 and 70 ppm, respectively, the soluble

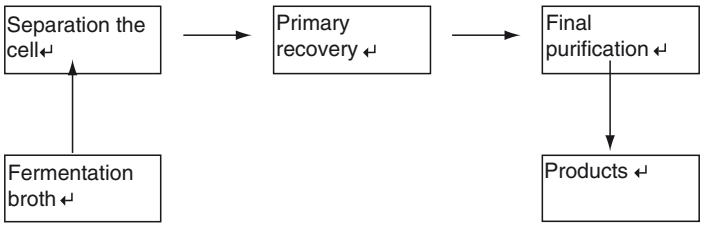


Fig. 8 General process for the PDO separation and purification from the fermentation broth

protein in the broth decreased to 0.06 g/L, and the recovery ratio of the supernatant liquor to the broth was greater than 99% (Hao et al. 2006). The second step is the removal of impurities and primary separation of PDO from the fermentative broth. The last step is final purification of PDO by vacuum distillation and/or preparative liquid chromatography. Many methods have been studied, for example, using evaporation for removal of water, ethanol, and acetic acid, electrodialysis for desalination, alcohol precipitation, and dilution crystallization for removal of proteins and salts, solvent extraction and reactive extraction, ion-exchange chromatography, adsorption with activated charcoal or a molecular sieve, and pervaporation with a zeolite membrane (Roturier et al. 2002; Wilkins and Lowe 2004; Adkesson et al. 2005; Cho et al. 2006; Malinowski 1999; Ames 2002; Sanz et al. 2001; Gong et al. 2004; Malinowski 2000; Hao et al. 2005, 2006) Although several methods have been developed for the separation and purification of PDO, disadvantages also exist. For example, the energy consumption of evaporation and distillation is high; the loss of PDO, leading to a low PDO yield during electrodialysis and the membrane pollution, can be very serious; and the energy consumed using chromatography is even higher than that consumed using simple evaporation and distillation because the PDO solution is diluted and the resin or adsorbent has low selectivity and capacity. Many extractants have been studied for liquid–liquid extraction of PDO but no effective extractant has been found for hydrophilic PDO. The process of reactive extraction is complicated and the trace amount of aldehyde in PDO is prohibitive for polymerization of PTT, which is difficult to control.

The methods and technologies studied so far have their limitations or drawbacks in terms of yield and energy consumption. For further development, classic separation techniques need to be improved or combined with other new technologies for PDO to be produced on a large scale.

4 PTT Production with PDO

PTT was first patented in the 1940s, but the high costs of production of high-quality PDO, the starting raw material for PTT, became a hindrance to industrialization of PTT. It was not until the 1990s that commercial production of PTT was possible,

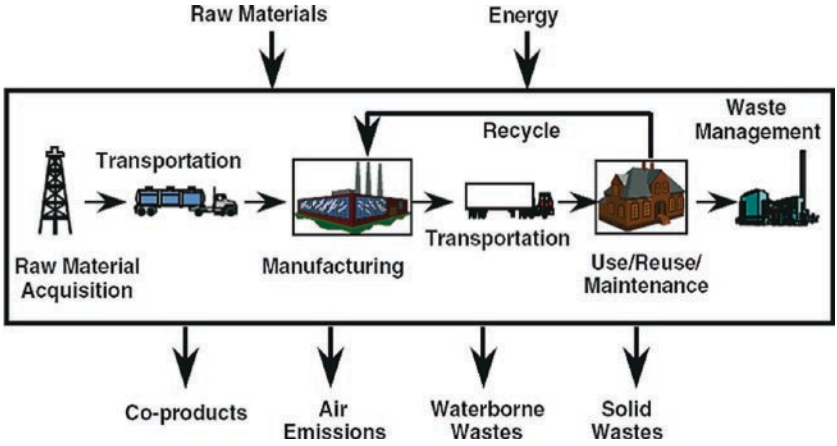


Fig. 9 Product life and environmental effects of poly(trimethylene terephthalate) (PTT) (Kurian 2005)

when Shell Chemicals developed a method of producing PDO at low cost. With the development of microbial PDO production, the PTT synthesized with microbial PDO has received much attention from researchers.

Sorona, a PTT polymer produced by DuPont with microbial PDO, can be easily modified to achieve desirable functional properties as well, i.e., excellent physical and chemical properties, dimensional stability, low moisture absorption, easy care, good weather resistance, easy processability, and recyclability. It has been shown to have advantages over other polymers, from the raw material to ultimate disposal when considering the effect on the environment (Fig. 9). For example, greenhouse gas emission in the manufacture of bio-PDO has been demonstrated to be about 40% less than for petrochemical PDO; the overall PTT polymerization process is more energy efficient than for PET; polymerization and downstream processing of Sorona uses less energy compared with PET owing to the lower temperatures required, both for processes involving remelt and for dyeing; and recycling of Sorona is made much easier by the absence of heavy metals in the product, compared with PET and nylon (Kurian 2005).

Therefore, PTT produced with microbial PDO will have promising applications in the near future in fibers for apparel and carpets, films, and engineering components, which will significantly enlarge the scale of PDO production.

4.1 Introduction to PTT

PTT is a semicrystalline polymer synthesized by the condensation of PDO with either terephthalic acid or dimethyl terephthalate. The unique, semicrystalline molecular structure of PTT features a pronounced “kink”, as shown in Fig. 10

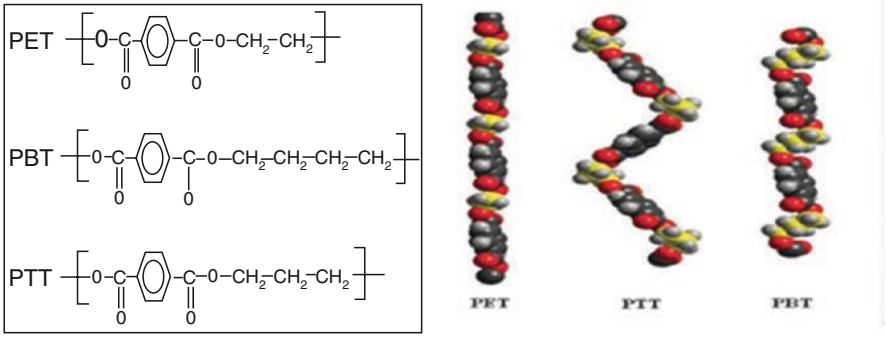


Fig. 10 Molecular formulas and semicrystalline structure differences of poly(ethylene terephthalate), PTT, and poly(butylene terephthalate)

(Hu et al. 2008), which gives serious beneficial properties to PTT compared with PET and PBT.

The molecular structure of a zigzag shape can translate tensile or compressive forces at a molecular level to bending and twisting of bonds rather than simply stretching, which is analogous to the tensile behavior of a coiled spring compared with a straight wire. So PTT shows better stretch-recovery characteristics than other traditional polymers. Also other properties of PTT are between those of PET and PBT, such as the crystallization rate and glass-transition temperature. Hence, engineering plastics is probably an important application field of PTT.

4.2 The Production of PTT

PTT is a semicrystalline polymer synthesized by the condensation of PDO with either terephthalic acid or dimethyl terephthalate, followed by polymerization. Studies of PTT had never gone beyond academic interest until recent years because one of its raw materials, PDO, was very expensive and available only in a small volume. PTT received less attention compared with PET and PBT. However, recent breakthroughs in PDO synthesis made PTT available in industrial quantities, thus offering new opportunities in carpet, textile, film, packing, and engineering thermoplastics markets.

The polymer production is similar to the PET synthesis and involves direct esterification and ester-interchange polymerization (Fig. 10). For PTT, Shell Chemicals developed a low cost method of producing high-quality PDO, the starting raw material for PTT. There are two routes to synthesize PTT, namely, the transesterification of dimethyl terephthalate with PDO and the esterification route with terephthalic acid and PDO. In the first stage of polymer synthesis, terephthalic acid or dimethyl terephthalate is mixed with PDO to produce oligomers having one to six repeat units with the help of a catalyst. In the second stage ,this oligomer is

polycondensed to a polymer with 60–100 repeat units. The catalyst used in the first step also accelerates the polycondesation reaction. Generally, this objective can be fulfilled by two methods. The first is the use of a lower process temperature, which reduces the processing time in the melt phase to a minimum and keeps oxygen out completely. The second way involves selecting a sufficient amount of a catalyst and adding stabilizers such as phosphorus compounds or sterically hindered phenols.

4.3 The Properties of PTT Made from PDO

Although PTT was first synthesized by Whinfield and Dickson in 1941, it was never commercialized because of the lack of an economical source of trimethylene glycol monomer. Recently, Shell Chemicals announced the development of a technology to make trimethylene glycol economically via the hydroformylation of ethylene oxide. With a cheap monomer source, it is now possible to commercialize PTT at a competitive price. PTT has an odd number of methylene units between the terephthalate moieties, in contrast to PET and PBT, which have even numbers of methylene units. PET molecules are more fully extended. Two carboxyl groups of each terephthaloyl group are situated in opposite directions. Also, all bonds are in the *trans* conformation, with successive phenylene groups at the same inclination along the chain. PTT differs from this conformation with bonds of the $OOO(CH_2)_3OOO$ unit having the sequence *trans–gauche–gauche–trans*, leading to the contraction of the repeating unit and, because of the opposite inclinations of successive phenylene groups along the chain, the molecule takes on an extended zigzag shape.

As a promising polymer, PTT's trimethylene units are organized in a highly contracted and helically coiled *gauche–gauche* conformation. PTT nanofibers exhibit high surface smoothness, length uniformity, and mechanical strength. PTT fiber opens up an avenue for novel optical fibers for wavelengths ranging from the visible to the near infrared, and they can be arbitrarily positioned, bent, intertwined, twisted, tensed, and assembled into different structures.

PTT's outstanding resilience, relatively low melt temperature, and ability to rapidly crystallize offer potential opportunities for its use in carpet, textile, film, packing, engineering thermoplastics, and other marketplaces, particularly those dominated by nylons, PET, and PBT. In addition, it is reported that the promising aromatic polyester PTT can be enzymatically hydrolyzed using diverse enzymes.

4.4 The Market and Applications for PTT

PTT was first synthesized in 1941, but owing to the high costs of high-quality PDO, one of the raw materials to produce PTT, it was not commercially available.

In 1998, PTT was finally introduced to the market by Shell Chemicals under the trade name Corterra, since an economical process for the production of PDO had been developed. PTT fibers are commercially produced today by DuPont and Shell. PTT has special characteristics as a fiber. It is particularly interesting in carpet fibers, where it has shown outstanding resiliency and chemical resistance. Also, this polymer shows potential in the field of engineering thermoplastic polymers and fabrics.

PTT was introduced as a commercial aromatic polyester polymer, joining others such as PET and PBT. This semicrystalline polymer is produced industrially by the condensation of PDO with either terephthalic acid or dimethyl terephthalate. The breakthroughs in PDO synthesis have made it available in industrial quantities, and this offers new opportunities for the carpet, textile, film, packing, and engineering thermoplastics markets.

The applications of PTT in the textile industry include filament yarns, staple fibers, and bulked continuous filament yarns for carpets. In blends with other synthetic fibers such as Lycra or natural fibers such as cotton, PTT enables a variety of end products to be produced that have a soft feel, good drape, and good stretch and recovery qualities (Carr et al. 1997; Yonenaga 2000; Dupeuble 2001; Kathiervelu 2002). One of the most recent applications of PTT is sewing thread which will endow clothing products with added value by appropriate extensibility, recovery, and dimensional stability. The extraordinary properties of PTT are very useful for sports and leisurewear as well as elastic interlinings and shirting fabrics. The wear performance of carpets made from PTT is equal to or better than that nylon, without the staining or cleaning problem. PTT has exhibited very good performance in apparel: softness, stretch, and brilliant lasting colors in both knit and woven fabrics, in hosiery and intimate apparel, linings, denim, swimwear, etc. Another application of PTT is upholstery because of its good stretch recovery, dye and print capability, stain resistance, and resiliency.

5 Outlook

Although polyester polymers have been known for a long time, the world polyester market is still growing. More and more new applications are under development. This has many causes. In contrast to many other polymers, recycling is easy. Polyesters contain only carbon, hydrogen, and oxygen. For these reasons it is likely that the use of PDO will grow at a high rate in the next few decades. The bio route is a very interesting future option. The realization of this route depends on the progress of process development to obtain fiber grade quality PDO and the carbohydrate to oil price ratio. If the whole cost of PDO production by the biological method were decreased to a level to compete with that of the chemical method, through development of the separation and fermentation technology, the PTT produced by microbial PDO would have good prospects.

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