

# Chapter 8

## Response of Society and Market



### 8.1 Society and Plastics

Plastic polymers have benefited the human society and heavily contributed to our improved style of life from several viewpoints. Indeed the easy processable, light and low-cost structural plastics and the possibility of combining them in materials with functional and thermomechanical properties have allowed a rapid growth for easy and large-scale production with advanced performances in all fields from building and construction, electronics, packaging and transportation industries as well as to the activities addressed to the biomedical assistance for human health. No doubt that this trend will continue and will certainly be assisted and promoted by developing new strategies to produce plastic polymers from renewable sources when this is sustainable.

Packaging sector is the industry that has the greatest consumption of plastic, thanks to the versatility of the material able to respond to different needs. Depending on the degree of protection necessary to preserve the shape and properties of the packaged object (also perishable, such as food), the plastic used can be rigid and tough or if the packaging must be convenient to goods transportation one can choose a more flexible plastic or a combination of the two packages. The packs can have any shape, size and colour. Plastic packaging helps also to keep people healthy in a number of ways. It is used for medical facilities, to store a variety of solid and liquid goods of regular home use.

Plastic (and more generally polymers) plays a significant role in the building and construction industry. In fact, the construction industry is the second largest consumer of polymers used in items such as pipes and valves. These goods have superior resistance to corrosion with respect to traditional materials (generally provided by metals and alloys) and can be used for fresh water (cold and hot), but even for oil and in some cases for saltwater. In addition, some decorative and attractive elements including bathroom units, floors, pipes fittings, plumbing fixtures, insulating panels, banisters, windows, doors, gratings and glasses are increasingly designed by using thermoplastic polymers. Polymers are the main components of paints for exterior

and interior (Ali et al. 2013). Made of plastic is the garden furniture such as tool sheds (recently produced also in composites with cement and wood fibres), toys for children, tables, chairs, deckchairs, armchairs, lamps, pergolas and canopies. With this regards, it is important to mention that polymers and plastics are generally less expensive, even if the cost of such furniture is strictly depending on the design. Thanks to thermal and insulating properties, plastic is ideal for use in house wiring generally passing corrugated pipes in walls or floors.

Plastic is nowadays widely used in domestic environments, especially for small appliances such as food processors, microwave ovens, toasters, mixers, coffee makers, irons, vacuum cleaners, small mixers, razors and hairdryers. Plastic foams are used in refrigerators for insulation, while the interior is made of plastic that is durable and easy to clean. In dishwashers, dishware racks and water diffusion blades are made of plastic. The use of these plastic elements in the listed electric households makes these last particularly durable and allows saving energy considerably. Also, plastic allows making smaller computers possible by allocating all of the electronics necessary within a dust-free and well-insulated environment where miniaturization was possible thanks to the use of plastic.

Evolution of modern transportation was also markedly supported by plastic materials thanks to the toughness, resistance to corrosion, durability, lightweight and easy dyeing. In particular, in the use in automobile, plastic and polymers saved million barrels of petrol owing to weight decrease of passenger cars.

Likewise, in the field of public transport, with particular reference to aircraft, trains and buses, the increasing use of polymers and plastic (seats, engine parts, wiring, roofing/interior and exterior panels, floors, windows and portholes) has made these mass transport tools cheaper and even lighter. This results in improved aerodynamics, which leads to better fuel efficiency and performance and generates a reduction of fuel consumption. Plastic can be used in part of helicopters because rigid and durable, but even flexible enough to withstand the vibrations.

Plastic and more generally polymers have entered powerfully as the main materials in all consumer goods used in sports activities: from motorcycles to bicycles (for outdoor or gym), canoes, skateboards, skis, gymnastic equipment, tennis rackets, sports clothing with particular reference to increasingly performing and engineered shoes. The plastic, in addition to being used for everyday objects or almost, has found advanced applications in radar systems because it allows the passage of waves and in some aerospace technological applications as, for example, in apparatus of space shuttles (such as the ablative shields necessary for re-entry).

The above helpful applications were first realized with polymer produced from fossil and mostly characterized by long durability (Pereira et al. 2013). In the absence of rules and control about disposal this has created problem to the environment as dismissed items, if freely abandoned in the environment, can withstand for long time producing mostly an aesthetic pollution which can also become dangerous. Clearly, this is a very moderate problem for more durable and higher cost items but is typically a problem for packaging, which is by the way the largest application field.

An approach to relief this problem comes from biodegradable plastics, which can be disposed in the environment and disappear in much shorter time than traditional plastic does. Clearly, these products cannot be used for practically all the other uses summarized above.

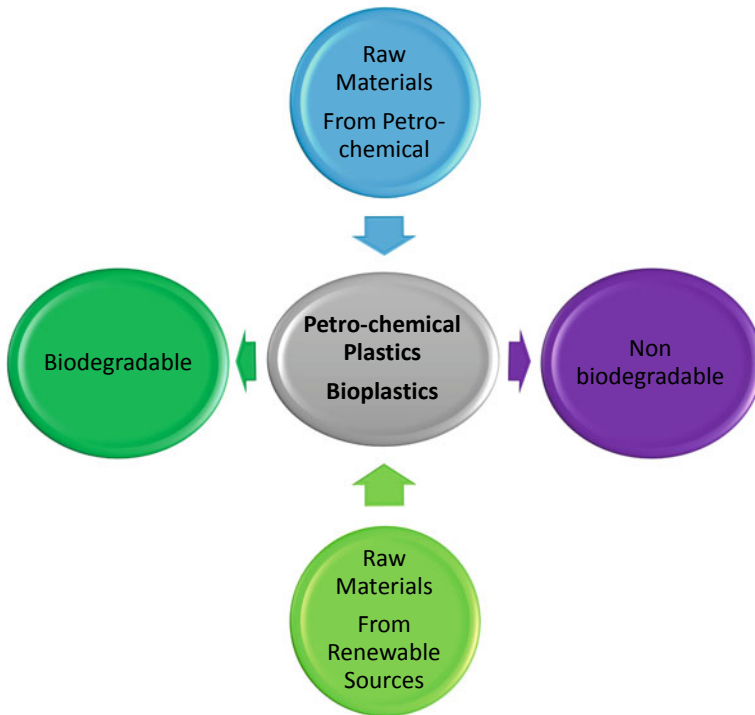
The biodegradability has also attracted the attention towards plastic from natural and then renewable sources thus helping to save oil and introduce more natural technology.

As discussed in this chapter, the term bioplastic includes today a series of polymeric materials where a significant weight part derives from renewable sources, but the final properties are not necessarily different from those of the analogues from fossil sources. Rather, apart the biodegradability necessary in some applications (agriculture, biomedical material and some very short-term packaging) the objective is to reach comparative properties. In this framework, the modern idea of circular economy, which claims recycling to zero waste, and the availability of raw materials in the necessary quantity put forward additional concepts in evaluating the comparative use of plastics and bioplastics.

## 8.2 Available Raw Materials

From the previous introductory section, it may result that today, and particularly in the future, the most relevant property for sustainability and then low environmental impact can be identified in the origin from renewable sources, whereas properties such as biodegradability will be requested only for some short-term application and when the collection for recycling is not possible. Indeed, the scheme below provides a synthetic but clear picture of the relationships between raw starting materials and final product related to plastics and bioplastics. It appears that the origin is clearly different but the functional properties, biodegradability taken as reference, are not strictly related to the origin. Therefore, one can say that on one side similar structures and properties can be reached from both renewable and fossil organic compounds, while the final application remains open to both. Conceptually, bioplastics allow saving resources, as the used raw materials are renewable. On the other side, fossil raw materials are not regenerable and it is necessary to consider the recycling a very efficient way of saving resources for long life materials of the latter type.

In an integrated view of sustainable materials displaying plastic behaviour, it is today possible to tell that in principle man is capable to produce the large variety of molecules for any distinct properties from different types of raw materials either from fossil or renewable sources (Fig. 8.1). For this purpose, the fossil oil and its refining supply a number of hydrocarbon compounds as convenient starting feed for chemical synthesis of monomers, which are then converted in a number of plastics by industrial polymerization processes. On the other side, nature with its cycles is constantly producing renewable organic molecules: some of them are already in form of biopolymers and can be converted into bioplastics by formulation, others are building block to be used by man for preparing either new plastics or the same



**Fig. 8.1** Different origin and property comparison of bioplastics and plastics

plastics as those from fossil origin. Plastic materials both obtained by formulation containing nature-made biopolymers and by polymerization of monomers from bio-raw materials are classified as bioplastics. Raw materials from any origin are not only used for making plastics, but suffer from strong competition by other applications. It is necessary to note that oil and natural gas come from ancient organic materials compressed under heating over geological time and are not renewable in a human time scale; its reserves are roughly estimated at around 130–200 billion tons, which can increase to 500–600 billion tons with oil sands (for the moment not extracted for technological and economic issues). By considering that the consumption is currently around 3–5 billion tons per year, reserves wear out in approximately 30 years for oil and 100 years if technology will be able to recover oil from sand. Even if oil consumption for plastics polymerization, formulation and processing is in the order of some percent of the global oil consumption, in the general context of consumption related to human activities, it actually suggests to find alternative sources for the synthesis of plastics in order to have a beneficial effect on the future availability of this fraction of oil that could be used for different applications and thus by replacing crude-oil-sourced polymers with non-fossil materials.

It is well known that agricultural potential on the Earth is limited by the competition with food crops. Therefore, raw materials should be selected among agricultural, urban or industrial waste or secondary products from food and/or agricultural indus-

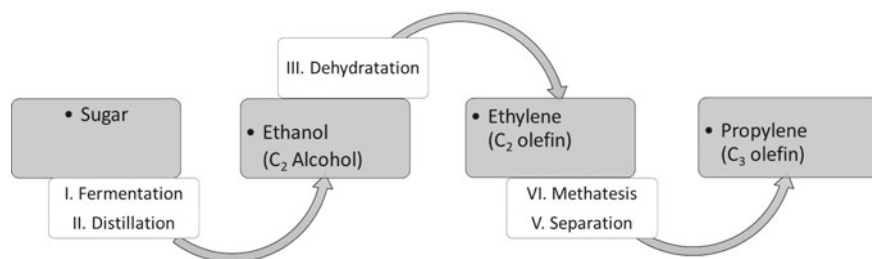
tries (biomass) or carbon dioxide known to be ‘greenhouse gases’ which could be conveniently converted into chemicals useful for the plastic industry. The conversion processes of these raw materials into bio-monomers and bio-blocks to replace those of petrochemical derivation can follow microbial, chemical, mechanical or genetic methods. At the end of the process, i.e. after conventional polymerization, finished products are similar to the raw materials or plastics based on petroleum. Renewable sources are the most promising solution if the so-called renewal period is of the order of one or a few years, exceptionally of several tens of years as it happens for wood. Biomass (especially waste from the food industries), but also agricultural products not dedicated to the food industry (such as wood) are generally rich in chemicals, monomers, oligomers and polymers. As such, they can be a promising natural resource for polymers, reinforcements and additives for direct use or after physical, chemical or microbial treatments.

Monomers and polymers from renewable sources, bio-based building blocks, are now subject of activity of several chemical industries even if the quantitative availability is far below that necessary to replace the raw material request at present satisfied by fossil sources. There is no well-identified process that can provide a uniform supply to chemical industry and in particular polymer industry. In addition, the polymerization processes provide for a significant chemical differentiation of the building blocks necessary for the production of materials with the standard properties and performances required by the market. The above biomasses used as renewable resources already foresee a very significant differentiation in the chemical substances that can be extracted both from plants and in general from agricultural products or by-products and this aspect should be taken into serious consideration in future developments of the chemical industry and polymers. The aforementioned differentiation in materials from renewable resources is confirmed by recent progress in the sector.

Some examples are given below to comment and inform about the natural resource building blocks used at present for the production of bio-related plastic materials to provide evidences about the possibility offered to the human society for producing useful materials without consuming fossil resources. At the same, we mention the presently available synthetic routes leading to bio-related polymers for plastics while the already formed bioplastics derived from nature were reported in Chap. 5, even if more details and information outside the purpose of this book can be found in the literature cited at the end of the present chapter (Ali et al. 2013; Chen 2014; Kang and Lee 2015; Park et al. 2017; Pereira et al. 2013; Raj et al. 2008; Scarlat et al. 2015; Wagner 2014).

### ***8.2.1 Monomers from Alcohols***

Fermentation of sugars from renewable sources can be directed towards ethanol which can be easily converted to ethylene, thus providing a way to produce by conventional polymerization bio-originated polyethylene. The ethylene derived from the



**Fig. 8.2** General processes scheme of ethylene and propylene preparation from sugars

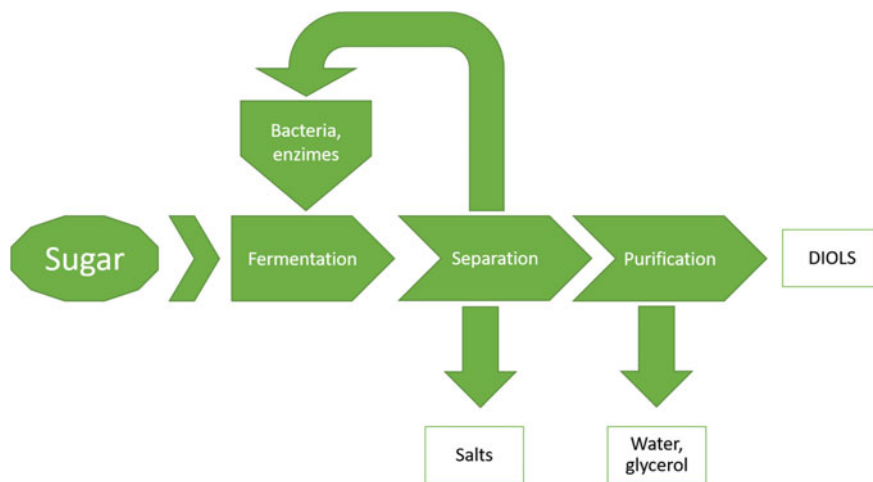
fermentation of biomaterials can be converted by metathesis to propylene, according to scheme shown in Fig. 8.2.

Again, the propylene produced according to this process can be also polymerized to isotactic polypropylene. This process, already described from another viewpoint in Chap. 5, is here mentioned for having a complete coverage. Industrially, PE from sugar cane ethanol is produced since September 2010 by Braskem in Brasil which is world leader with an annual capacity of 200 Ktons. Total Petrochemicals, IFP Energies Nouvelles (IFPEN) and Axens announced an alliance to develop a new technology for the production of ethylene by dehydration of ethanol. Dow and Mitsui also have an ethanol-to-ethylene plant and a polymerization plant. Clearly, both ethylene and propylene obtained accordingly can be converted into the corresponding homopolymers as well as in the useful copolymers by the same catalytic processes used for the same monomers derived from fossil oil. This route therefore does not produce an alternative material to two important polymers, polyethylene and polypropylene from fossil, but rather the production of the same polymers from renewable sources.

### 8.2.2 Monomers and Building Blocks from Diols and Polyols

Fermentation of renewable biomaterials can be directed towards various diols through a fermentation enzyme assisted route as described in the very general scheme reported in Fig. 8.3.

Microbial-based 1,3-propanediol can now be produced with a method competitive with traditional technologies utilized to obtain this compound from fossil 1,3-propanediol. This allows replacing to an important extent the same compound from fossil origin in the manufacture of polymers with plastic properties such as polyesters and polyurethanes. The biotechnological route passes through glycerol produced by cleavage of natural fats, which is available in large amount as waste in the biodiesel production. The process is based on the conversion to 1,3-propanediol by the microbic action of *Citrobacter*, *Klebsiella*, *Lactobacillus*, *Enterobacter* and *Clostridium* strains.



**Fig. 8.3** General scheme of diols production via fermentation of natural products

An additional industrially relevant diol is 1,4-butanediol (BDO). The BDO production is an emblematic example of how the future of chemistry should evolve, not only because it will use renewable raw materials and especially genetically modified enzymes but also because it is currently one of the chemical products synthesized from all the raw materials possible alternatives to oil. Now Genomatica has developed a commercial bioprocess for the production of BDO from dextrose. The sustainable bioprocess was successful and was developed by selecting a strain of *Escherichia coli*; the results have led to such a high level of performance that an integrated technological platform has been developed providing for the engineering of the enzyme, and of the metabolic process of the organism, as well as for the development of an effective fermentation and recovery processes downstream. This allows to use bio-generated BDO instead of the same compound from fossil; BDO is one of the key building blocks to make polyurethane and co-polyester. The major uses of BDO are in the production of polybutylene terephthalate and polyurethane fibres and intermediates such as  $\gamma$ -butyrolactone (GBL) and tetrahydrofuran (THF). THF is used as raw material for the synthesis of polytetramethylene ether glycol (PTMEG), monomer to produce elastomers based on polyurethanes and polyurethane fibres. Furthermore, in small part THF is used also as a solvent in the production of PVC. Recently, low molecular weight polytetrahydrofuran (PolyTHF) has been produced by BASF and goes out on the market for application as elastic fibres.

Moreover, other natural polyols or vegetable oil polyols, often generated by glycerol fermentation can lead to polyurethane foams, thermoplastic polyurethanes, polyurethane elastomers and unsaturated polyesters; all being considered partially bio-derived polymers or plastics.

### 8.2.3 Lactic Acid and PLA

Lactic acid is the monomer used for the production of the corresponding plastic polymers under the name of polylactic acids (PLA) already mentioned in the present book. The synthesis of this acid monomer can be performed either by chemical synthesis routes or by fermentative production routes. The former produces the racemic 1 to 1 mixture of D- and L-lactic acid while the latter fermentative production allows the generation of optically pure D- or L-lactic acid when the appropriate microorganism is selected. Almost all lactic acid is today produced by the fermentative route, starting in general from corn-derived dextrin. Two processes are generally used, namely, the homofermentative route converting a hexose molecule into two lactic acid molecules, or the heterofermentative process which gives one mole of lactate from one mole of glucose as well as CO<sub>2</sub> and acetic acid or ethanol. Some basic information are given in Table 8.1.

The fermentation starts, indeed, from cheap renewable raw materials, but suffers from low productivity due to long conversion times and low active cell concentrations. The fermentation procedures using high cell densities or cell recycling have been recently shown to achieve high lactic acid productivity. Additional improvement comes from the integrated-membrane fermentation reactor, a system able to reduce the supplied raw material need. Several different substrates, apart from pure sugars and food crops, can be used for lactic acid production with advances in process engineering as reported in Table 8.1.

Also, lignocellulosic, starch biomasses, dairy by-products, agro-industrial and food wastes, glycerol and algal biomass can be used for the fermentative production of lactic acid. Commercial fermentation takes place in batches, with process conditions that provide a pH of around 6, temperatures of 40 °C and a low concentration of oxygen. The addition of calcium carbonate or calcium, magnesium and sodium hydroxides to the broth neutralizes the solution giving the corresponding lactate salt, which is soluble in the reaction mixture whatever the counterion. The fermentation broth is then filtered to remove bacterial cells and other insoluble impurities. The purification takes place through separation techniques such as ultra- and nanofiltration, electro dialysis or ion-exchange processes. The major problem associated with efficient lactic acid fermentation is related to the end-product inhibition. The removal

**Table 8.1** Lactic acid from bacteria-assisted homofermentative and heterofermentative process

Materials and results	Homofermentative process	Heterofermentative process
Starting feed	Hexose, Pentose	Hexose, Pentose
Bacteria	Lactococcus, Streptococcus, Pediococcus, Enterococcus	Leuconostoc, Oenococcus, some Lactobacillus species
Products	Lactic acid (good purity)	Lactic acid, ethanol, acetic acid, and carbon dioxide
Industrial meaning	Sustainable thanks to high selectivity	Problems of monomer purification



of formed lactic acid during fermentation has resulted in a 50-fold enhancement in cell concentrations with dialysis membranes. Lactic acid derived from fermentation can be obtained almost entirely in the form of the isomer L. From lactic acid, the polymer can be produced by polycondensation with azeotropic condensation which does not require the use of external agents for the elevation of the molecular weight. The method requires a high aprotic solvent, temperature around 130 °C and reaction time of 30–40 h.

As reported in other sections of this book (Sec. 5.4), the PLA can also be obtained from the dimeric lactide by ring-opening chain polymerization with the assistance of catalyst.

### 8.2.4 Polyamides

Polyamides have this name as their macromolecules are formed formally by condensation of a carboxylic acid with an amino group to give an amido group through the elimination of a water molecule. The amido group,  $-\text{CO}-\text{NH}-$ , formed is part of the macromolecule backbone and interconnects monomeric units of which is part. The same functionality, called peptide group, is present in the biopolymers proteins, which, however, are not usually named polyamides. Indeed, the presence of a significant number of intra- and interchain hydrogen bonding in proteins do not allow a useful plastic behaviour. On the contrary, this is rather very typical in synthetic polyamides thanks to the significant separation between successive amido groups by long flexible aliphatic chains as for example, in nylon-6 where a linear chain of five methylene groups separates two successive amido groups.

One of the industrial route to produce plastic polyamides is based on the condensation of a diamine with a dicarboxylic acid as in the pioneer case of nylon 66 derived from hexane-1,6-dioic acid (adipic acid) and hexamethylene diamine, both from fossil origin.

Attempts to produce bio-derived polyamides were therefore based on the preparation of building blocks from renewable natural sources for finally obtaining the same plastic polyamides as from fossil, but saving resources. Accordingly, bio-polyamides are synthesized from two or more dicarboxylic acids and diamines. Triglycerides and the derived long-chain unsaturated acids present in vegetable oils can be converted into suitable bifunctional diacids which in combination with aliphatic diamines can be used for the production of polyamides by polycondensation processes. In this context, raw castor oil is hydrolyzed to give ricinoleic acid, which is then converted to sebacic (1,10-decandioic) acid by reaction with alkaline hydroxide at high temperature. 1,12-dodecanedioic is prepared from oxidation process of lauric acid catalyzed by yeast strain. These partially bio-derived plastic polyamides are an industrial reality, such as polyamide 6.10 Ultramid<sup>®</sup> balance (by BASF) based about 60% on the renewable raw material sebacic acid. Also, diamines are derived from renewable sources for the production of bio-polyamide; indeed, pentamethylenediamine and

tetramethylenediamine are naturally occurring substances produced by microbial biosynthesis by decarboxylation of the amino acid lysine and ornithine.

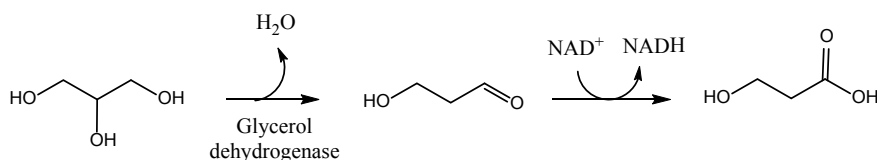
Interestingly, aminobutyric acid is originated from biomass fermentation and its polymer, unlike the other polyamides, is fully biodegradable by bacteria isolated from activated sludge.

### 8.2.5 Acrylic Polymers

Starting once again with glycerol, which is a largely diffused natural product and apparently one of the most used as raw source for different building blocks or monomers, it is possible to produce a precursor of acrylic acid today coming mostly from fossil. This precursor is actually the 3-hydroxypropionic acid (3HP), and can be obtained from glycerol according to the pathway reported in Fig. 8.4 (Raj et al. 2008). The successive dehydration produces the target monomer.

The bio-based acrylic acid has been proposed for use in the manufacture of super-absorbent polymers (SAP) used mainly in diapers (for baby or for adults) and other hygiene products. Clearly, there is a significant and impressive aspect towards the replacement of acrylic acid produced by oxidation of propylene derived from the refining of crude oil with acrylic acid from renewable resources, but we must emphasize that the monomer molecule and the polymer is the same with its advantages and disadvantages; the only difference being the origin which does not affect the ultimate properties. In any case, as acrylic acid is largely used even in copolymeric products, the developing and commercializing renewable acrylic acid is important as the present industrial production mainly depends on fossil fuel resources. Some recent non-positive economic evaluations have suggested to stop this route.

The most popular acrylic derivative with application in plastics products is certainly the poly (methyl methacrylate) (PMMA), which at the time of this book preparation is exclusively produced from fossil. Indeed, there are no sustainable routes to its obtainment from naturally occurring raw materials. When this happens, the recourse to natural sources implies a change of the polymer structure. In case of PMMA, a very interesting approach to reduce the environmental impact of the material from fossil has been achieved by blending PMMA with a compatible biopolymer, and in this case the PLA. The resultant blend features are lower processing temperatures, greater melt flow properties and reduced carbon footprint, as up to 25% PLA is added. It is



**Fig. 8.4** Preparation of 3-hydroxypropionic acid from glycerol promoted by enzymes

important to stress that the blend material maintains the good and requested property characteristics of neat PMMA. Clearly, the new blends are not exactly the same also from plastic viewpoint as indeed PMMA is an amorphous material with  $T_g$  close to 90–100 °C, PLA can be amorphous with lower  $T_g$  at around 60 °C, while the possible presence of a crystalline phase would imply a melting point of 160 °C. Thus, the morphology and thermal behaviour of the blend must be controlled for appropriate application.

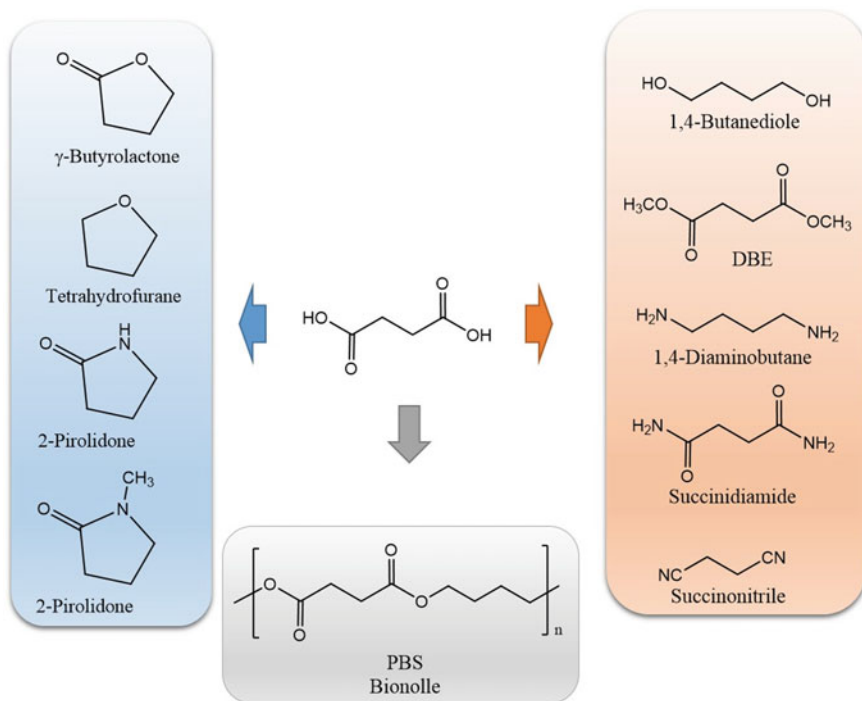
### ***8.2.6 Other Bio-derived Building Blocks for Plastic Polymers***

This section has the purpose to introduce a very significant aspect of the structure to property relationship in plastic polymers which can be profitable for reducing the environmental impact of these materials.

This aspect is alternative to the obvious approach based on the development of a preparative route for the obtainment from natural resources of a monomer or polymer presently from fossil. In this case, nothing changes in the properties and use of the final material with the additional positive result of saving resources. This complete substitution is not always possible and the approach for saving resources towards improved bio-derivation can be achieved by a partial substitution of the material with building blocks from nature or by compatible blending of a fossil polymer with a bio-derived polymer (as above described in the case of PMMA).

An additional example about the possibility of this chemical differentiation related to naturally derived molecules is provided by succinic acid as a versatile starting material. Figure 8.5 shows several useful molecules which can be prepared from this acid, in turn, obtained from renewable plant sugars. The succinic acid production in nature was extensively studied and related to several enzymes, namely, PEP carboxykinase, malate dehydrogenase malic enzyme, fumarase and fumarate reductase. Theoretically, 1 mol of  $CO_2$  is required to form 1 mol of succinic acid.

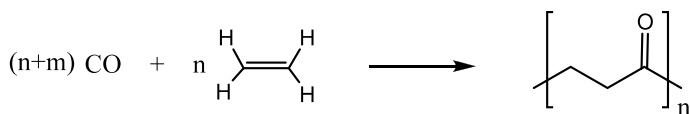
Succinic acid from natural resources, according to the concept to replace polymer building blocks, contributes to greener polymers as reducing the use of non-renewable sources. A significant example is provided by poly(butylene succinate) (PBS), which is prepared by condensation of succinic acid with 1,4-butanediol. Both starting molecules can be now obtained from natural sources. The polymer PBS is clearly a synthetic material invented by man, but thanks to recent efforts it can now be fully produced with starting materials of bio-origin. Furthermore, thanks to its molecular structure it is also biodegradable. Therefore, PBS presents an illuminating case of clever combination of the inventive technology with the use of natural resources. It is not a biopolymer, but certainly a bio-derived synthetic polymer with good properties with respect to performances, application and environmental impact. Then it is used successfully in biodegradable packaging films and disposable cutlery and its market is expected to increase with the green succinic acid process improvement. Also, it is predictable and partially already done that the bio-derived succinic acid can help to reduce the carbon footprint of commercial polyesters, polyols and



**Fig. 8.5** Various building blocks obtainable from succinic acid

polyurethanes currently produced from succinic acid obtained from fossil sources. Also, succinic acid allows the production of bio-chemicals like pyrrolidones which, in addition to be used also as green solvents and eco-friendly chemicals, is the base molecule for the preparation of vinyl pyrrolidone that is converted successively in a useful water-soluble polymer. Figure 8.5 shows that succinic acid is certainly very useful and versatile for use as a building block in a variety of bio-derived polymers, with the same or innovative structure with respect to analogues from fossil. All molecules shown in that figure and derived from succinic acid can be replaced by the same molecules of bio-origin when starting their preparation with succinic acid from natural sources. Bacterial strain and glycerin or glucose are the feedstock for the production of succinic acid that many, more or less bio-oriented, companies are today worldwide exploring and realizing to expand the market of succinic acid starting from a variety of biomaterials from plants.

In the search of new processes for the production of building blocks from natural sources, there are several issues to be considered if the objective is to replace already existing plastic polymers derived from fossil and with a well-acquired market share. These issues regard the availability of raw material, the processes for the industrial production of the useful molecules and their polymer and the ultimate properties of the prepared polymers.



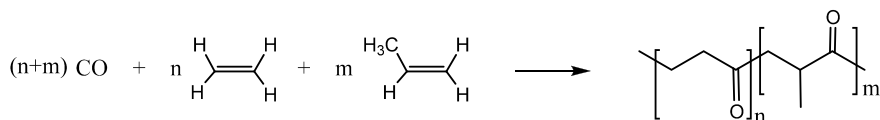
**Fig. 8.6** Copolymerization of carbon monoxide with ethylene to the corresponding alternating copolymer with polyketone structure

As far as availability and collection of raw material are concerned, the situation is made complex by the fact that starting plants derive from different types of agricultural productions and thus have different composition. The useful properties are present in different components that need to be separated and, in general, the transportation of the material to be used as feed in the industrial plant is necessary. Indeed, these feed materials are more differentiated and less treatable than oil and this implies a sort of molecular differentiation already at this level. The sustainable large-scale production of bio-derived building blocks for the chemical industry and the related market of plastic polymer is strongly dependent on a solution of this challenge. The processing of raw materials to products can certainly profit of the many advanced technologies discovered and applied by man for the conversion of oil in monomers and their polymers, even if some significant changes will be necessary as a much lower recourse to vapour phase is expected. Polymers with their complex structure and possibility to obtain similar properties from different molecular system may alleviate the above problems. Also, we have seen how sometimes the bio-derived building block has the same exact structure of the material from fossil. Polyesters as seen above, and also polyols and polyurethanes with properties comparable to those of petroleum-based analogues have been prepared from vegetable oils and their derivatives. However, building blocks from vegetable oils and their derivatives still face technical and/or cost barriers and the varied composition makes difficult to obtain polyols with consistent properties. Better collection and selection of starting materials from vegetable oils could allow the use of single components with more homogeneous structures and consistent ultimate properties.

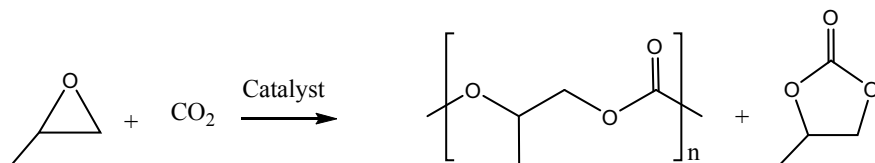
The last mentioned challenges encountered when using fully renewable carbon sources are markedly overcome in case of use, as starting materials, of carbon monoxide (CO) and dioxide (CO<sub>2</sub>), that are abundant by-products of human activity. These C1 molecules clearly can be converted into useful products only if man-made processes are used. The first example was provided by the production of linear polyketones from CO or polycarbonates.

Homopolymerization of carbon monoxide was not obtained yet, but CO can be efficiently copolymerized with alkenes to alternating copolymers where the CO is incorporated in the macromolecule backbone. The copolymerization of ethylene with carbon monoxide in the presence of palladium catalyst proceeds as depicted in Fig. 8.6.

New polymers with different physical and chemical properties can also be obtained by a proper selection of a mixture of alkenes. Indeed, the same catalyst used for ethylene and carbon monoxide copolymerization can be used for higher monoalkenes,



**Fig. 8.7** Synthesis of ethylene, propylene terpolymer–polyketone



**Fig. 8.8** Copolymerization of carbon dioxide with epoxides

also olefins. The property variation achieved by molecular differentiation can be approached also by terpolymerization starting with CO and two different olefins (Fig. 8.7). The introduction of structural disorder in the terpolymer allows modulating the thermomechanical ultimate properties of the produced polyketones.

The presence of carbonyl groups in 1–3 position along the macromolecular chains is responsible for strong intermolecular attractive interactions among polymer chains. As a consequence, the melting point and heat of fusion of polyketones are much higher than those of the corresponding polyolefins. Thus, poly(ethylene ketone) has melting point 290 °C, higher than linear polyethylene where the CO backbone groups are replaced by methylene groups. Polyketones have therefore higher tensile and impact strength than polyolefins; they also have remarkable abrasion resistance, very low water absorption, high barrier properties against fuel and oxygen, and good chemical resistance. Therefore, polyketones can be considered among high-performance engineering plastics. From the environmental viewpoint, the incorporation of CO in the alternate copolymer with ethylene indicates a saving of nonrenewable resources of 55% if ethylene from fossil is used and of 100% if ethylene from sugar fermentation is selected. Clearly, the polymer cannot be considered a biopolymer and it is not biodegradable, but certainly offers an interesting route to high-performing plastic material partially or totally derived from vegetables.

The same concept applied for olefin-CO copolymers was used by Novomer which developed a process for the production of polypropylene carbonate (PPC) by copolymerization of propylene oxide with CO or CO<sub>2</sub>. Polypropylene carbonate can be produced from propylene oxide, and carbon dioxide in the presence of various metal catalyst as reported in Fig. 8.8.

Again, the structure of the macromolecules originated from the formation of monomeric units derived by alternating combination of carbon dioxide with opened epoxy group. Therefore, each monomeric unit incorporates a molecule of CO<sub>2</sub>. Being propylene oxide also produced by fermentation, the final polycarbonate could be obtained totally from renewable sources. The same reaction can be applied to a number of different epoxides including various natural derivative products such as epoxidized soya bean oil, thus making the process significantly effective towards green plastic polymers.

### 8.3 Ultimate Properties for Distinct Applications

The main question to which this book is attempting to provide not an answer but just some partial understanding is: 'How far can bioplastics replace plastics from fossil origin?' Even if apparently all what is Bio is better than what is from Fossil, the examples and considerations reported in the previous chapters have certainly indicated that the answer to the above question is very complicated by the concurrence of many factors making impossible to provide a simple Yes or a simple No.

The main aspects to be considered in approaching the problem are technical on one side and economical on the other side. Both are time depending and can vary very rapidly in our times with the technology evolution becoming to grow asymptotically and difficult to control.

In this section of the chapter, we try to give some insights basing our consideration on the application performances of plastics and bioplastics where the only homogeneous and definite distinction is connected to the different origin.

According to the considerations reported in the previous chapters and the generally accepted definition, the term bioplastic applies to those materials with plastic behaviour that are derived from renewable natural sources. Then plastics from fossil and bioplastics can show similar properties and even the same molecular structure. The only distinct ultimate property is the biodegradability.

The present consciousness of the necessity to preserve the environment and its resources clearly would recommend saving, as far as possible, oil and natural gas and using material from renewable sources. This concept is much more effective in the case of energy production, but its validity certainly extends to all chemicals including plastics. The question that this section intends to approach is if the requested ultimate properties for plastics playing significant role in our life can be reached with feedstock from renewable sources, mainly vegetal.

This question is easily answered in case of bioplastics consisting of macromolecules with the same structure as the corresponding plastics from oil. The clear example is offered by the bio-polyethylene that is obtained by the same polymerization process as traditional polyethylene. In the former case, the monomer ethylene is obtained from bio-fermentation and in the latter case from oil, but the polymers are or at least should be identical as well as their final properties and applications. Accordingly, green polyethylene (PE) and green polypropylene (PP) claim, as understandable, full similarity, on all basic points summarized below and a remarkable contribution to preserve the environment.

- The production process is the same, for equipment, as for oil-based PE and PP.
- The polymer has similar properties to oil-based PE and PP, respectively.
- The polymers are also recyclable.
- The two polymers from fermentation reduce the greenhouse effect. It is possible to calculate that bio-derived PE helps to catch and commander 2.5 tons of CO<sub>2</sub> for each ton produced and 2.3 tons of CO<sub>2</sub> for each ton of bio-derived PP.

This example suggests that the easy way would be producing from renewable sources the same macromolecules for plastics as those presently used, at least those

demonstrated to be safe during use and recyclable. The new property to be introduced would be biodegradability when this cannot be avoided, as indeed it may be argued that recycling is more conservative and safe than degradation in the environment. Biodegradability is in any case an important additional property to consider and this requests development of new structures with respect to traditional plastics, which are presently considered to be too much long living; these good properties being converted into a drawback by the bad human use and incapacity to the correct disposal after use.

With these considerations in mind one should recall that nature is producing several important macromolecules such as polysaccharides, bacterial polyesters and proteins but their properties are far to be similar to traditional plastics and in addition to the not easy and not eco-friendly separation need additives to reach the requested ultimate properties. These additives must also be biodegradable and biocompatible to maintain this distinct feature. In general, these biopolymers are too rigid for providing viscoelastic response at room temperature and need the addition of significant amount of plasticizers to lower the  $T_g$  to the useful value, as in the case of starch. Others are not easy to be processed as traditional plastics, due to the unfavourable relation of thermostability to melting temperature.

As already reported in this book, several chemical building blocks are now industrially produced from renewable sources. Then it is predictable that a sufficient molecular differentiation can be reached also starting from renewable resources and, in principle, all useful and safe plastics can be in the future prepared without using fossil feedstock as an important contribution to saving natural resources and lowering the carbon footprint.

It seems reasonable that rather than looking to completely new structures from bio-origin having the marked requested properties, it is more convenient to approach the problem by replacing the fossil-derived plastics with bioplastics with the same or similar structure. This approach can also allow introducing better ecocompatibility and including biodegradability when strictly necessary, without excessive detriment of the ultimate properties.

Examples in this direction, in addition to the already mentioned PE and PP, are certainly available and have reached the market. One of such examples is provided by the so-called bio-PET (bio-polyethylene terephthalate) produced from plant-based ethylene glycol rather than petroleum-based ethylene glycol. In this way, while the 70% weight provided by terephthalic acid remains of fossil origin, 30% of the weight coming from ethylene glycol is from renewable sources. The ethylene glycol used in bio-PET is produced from agricultural activities and includes molasses, hay and bagasse. Bio-PET is used to make a number of useful industrial products such as drinking water and soda bottles. Products made from bio-PET have the same molecular structure as traditional and then the same ultimate properties. Bio-PET is widely accepted especially in the European and American markets and trusted by leading global drink manufacturers such as Coca-Cola (Japan). These products as the traditional ones must be submitted to strict measures in scrutinizing the production processes and quality control of products to ensure that they meet quality and con-



sumer safety standards. This has earned bio-PET various accreditations from leading global organizations such as the Japan Food and Drug Association.

The same route was also applied by several industrial producers for very common plastics such as polyamides (nylon) and polyurethanes.

## 8.4 Market Evaluation and Future Developments

There is no doubt that the increased concern for the preservation of the environment has reached the market thus promoting the utilization of renewable vegetal resources to ensure the consumption of carbon dioxide instead of the emission of CO<sub>2</sub>. This aspect is so important that one can also propose some price increase simply with this justification. Also, the consumer is ready to accept to a certain extent higher cost and lower performances if this is presented as the result of a more environmentally sustainable production route. These performances decay is evidently acceptable only for applications characterized by a low technology profile and where they do not arise any risk. An additional limitation may arise from the availability of raw material and the competition between application of crops for plastic polymers rather than for food.

The above very real consideration make rather complex to evaluate the real possibility of replacing traditional plastic materials from fossil with bio-derived material. The recourse to natural raw material also implies a revision of global market as the differentiation occurs not only during processing and synthesis as in traditional chemical industry, but already from the supply of raw material. Indeed, this last may be derived from different nature renewable products and then request different method of isolation and collection (Scarlat et al. 2015).

Worldwide attempts have pointed out that the consumption data broadly vary with sources, and the continuous technology evolution towards safer products independently of origin. Similarly, the larger sensitivity of the population to post-consume recycling of plastics which is becoming every day more effective in the concept of a circular economy may request to reduce material degradability. Production capacity of bio-derived plastic polymer could be not adequate to the market request for real difficulty of collecting starting material and the probability of increasing production cost to an extent that could hinder the diffusion in the market. According to market studies carried out by several international institutions, the consumption of bio-derived plastic polymer is expected to increase in the future (Table 8.2), but forecasts are variable in a rather broad range for the existence of the uncertainties indicated above.

Looking inside the numerical data in Table 8.2 it is interesting to evidence how different plastic polymers more or less bio-derived are requested by the market. According to European Bioplastics Society, the percentage is shown in Table 8.3 where the data were elaborated taking also into account the different bio-based content of different bio-derived plastics (Table 8.3), calculated by the following formula:

**Table 8.2** Global consumption of bioplastics from 2017 to 2022

Year	Consumption (million tons)	% Biodegradable of total consumption
2017	2.05	42.8
2018	2.09	43.5
2019	2.14	44.2
2020	2.19	45.5
2021	2.25	45.9
2022	2.44	44.5

Data source [www.europeanbioplastics.org](http://www.europeanbioplastics.org)

**Table 8.3** 2018 market shares of main bioplastics with the reachable bio-based carbon content

Type	Consumption as percentage of 2.05 Mtons (used in 2017)	Bio-based content %
Bio-PET + PTT	28.6	25.0
Bio-PE	10.2	100.0
PLA	11.1	100.0
Starch derivatives	19.7	Up to 85%
Others Biodegradable polyesters	12.7	Up to 50%
Bio-PA	12.5	Up to 50%
PHA	1.6	100%
Others	3.6	ND

$$\text{Bio-based content} = \frac{\text{Amount of bio-based Carbon}}{(\text{Amount of Bio-based Carbon} + \text{Amount of Fossil Carbon})} \times 100$$

An additional important analysis for a better understanding of the market potentiality of bio-based plastic polymers comes from the analysis of the Greenblue Organization that reports data about the differentiated market interest towards bio-derived and biodegradable plastic polymers also with reference to the related applications (Table 8.4).

The data of Table 8.4 demonstrate the market sensitivity to bio-derived properties. Thus, the biodegradability is not always appreciated, but depends on the application and seems to show a decreasing interest with years.

Increasing regulations and bans against fossil-derived and non-biodegradable plastic bags and other single-use plastic items promoted by Western Europe Countries are contributing to a significant extent to increase the demand for biodegradable plastics. According to new analysis from market research consultancy like IHS Markit, increased market value larger than 50% from 2018 to 2023 is expected in Europe.

**Table 8.4** Time evolution of biodegradable and non-biodegradable plastic polymers consumption in different applications

Year	Biodegradable polymer, %				Non-biodegradable polymer, %			
	Non-packaging	Flexible packaging	Rigid packaging	Total	Non-packaging	Flexible packaging	Rigid packaging	Total
2015	11.7	15.7	23.4	<b>50.8</b>	5.7	8.4	35.1	<b>49.2</b>
2020	8.5	6.0	11.5	<b>26.0</b>	9.2	3.2	61.6	<b>74.0</b>

Data from [www.greenblue.org](http://www.greenblue.org)

However, these evaluations are keen to be changed depending on the very variable analysis of the environmental impact made by experts and institutions, which may influence remarkably the public opinion (Wagner 2014). An example is provided by the regulations concerning food packaging, disposable tableware and bags sector which traditionally are the largest end-use segment. In this sector, some modern trend would recommend to avoid single use as multiple use reduces waste volume collection and may result to be more compatible with circular economy. In this case, biodegradability can be less important or better avoided. On the other side, the gradual expansion of composting infrastructure and the extended use of organic waste for energy production could act in the opposite direction.

The above data offer clear evidence that the prevalent interest for bio-derived plastic polymers was born from the need to avoid the long-lasting life of packaging dispersed in the environment by non-educated people and the lack of any sensitivity to recycling possibilities. We may argue that the situation is partially changed and while there is a strong interest in producing plastic materials from renewable sources, the biodegradability is not the only driving property. Rather the future attention may be more and more focused on producing from non-fossil sources plastic material having similar properties to the traditional ones (Chen 2014). Some examples were encountered already in the previous pages of the present book with monomers and building blocks from plants having the same or close molecular structure of the correspondent from oil. Also, the use of additional products from nature may provide a useful molecular differentiation more compatible with the environment thus making science and technology developed by man to work arm in arm.

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