Biopolymers, bioplastics, and bio-based plastics

In the chemical industry, together with petrochemicals and fine chemicals, polymers are some of the major products accounting, only in Europe, for more than 60 000 companies employing over 1.45 million people.

Almost a quarter of worldwide polymer production capacities are located in Europe; just considering EU-15 countries, the actual petrochemical polymer production is estimated at 15.4 million tons per year.

The substitution of petrochemical polymers with bio-based alternatives is actually considered as the necessary answer to the unacceptable environmental and social costs of petroleum-based and non-degradable plastics.

5-6% of the fossil oil is used to produce polymers/plastics
➢ European demand amounted to 47.8 million tonnes in 2014*

EU plastic industry:
> 60000 companies,
employing over 1.45 million people

Natural capital cost of plastics:
75 B$ per year (UNEP)

- ➢ **75% upstream impact** (extraction of fossil raw materials, manufacturing)
- ➢ **25% downstream (**end - life)

UNEP

PLASTIC IN COSMETICS

ARE WE POLLUTING THE ENVIRONMENT THROUGH OUR PERSONAL CARE?

PLASTIC INGREDIENTS THAT CONTRIBUTE TO MARINE MICROPLASTIC LITTER

*PlasticsEurope

Natural capital cost of polymers/plastics:
75 B$ per year

Solutions?

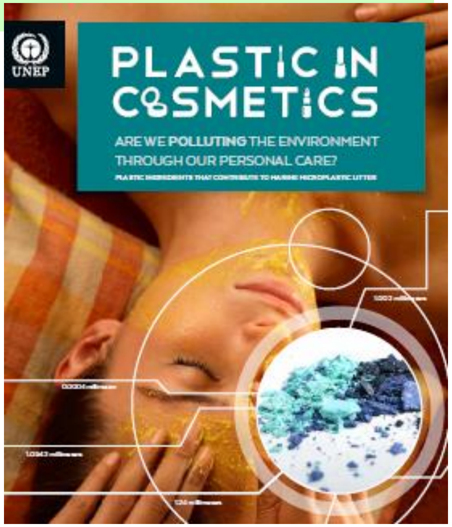
- ➢ efficient management of plastic waste
- ➢ more sustainable polymers/plastics

Trends?

Bio-based plastics market expected to reach 5.2 BEUR in 2030**

Challenges:

- ➢ **superior functionality**
- ➢ **competitive product price**
- ➢ **sustainable**



UNEP

PLASTIC IN COSMETICS

ARE WE **POLLUTING** THE ENVIRONMENT THROUGH OUR PERSONAL CARE?

[** www.industrial-biotechnology.eu](http://www.industrial-biotechnology.eu) (BIO-TIC – Non-Technological Roadmap)

theguardian

EU declares war on plastic waste

Brussels targets single-use plastics in an urgent clean-up plan that aims to make all packaging reusable or recyclable by 2030

Daniel Boffey *in Brussels*

Tue 16 Jan 2018 15.50 GMT

The EU is waging war against plastic waste as part of an urgent plan to clean up Europe's act and ensure that every piece of packaging on the continent is reusable or recyclable by 2030.

Following China's decision to ban imports of foreign recyclable material, Brussels on Tuesday launched a plastics strategy designed to change minds in Europe, potentially tax damaging behaviour, and modernise plastics production and collection by investing €350m (£310m) in research.

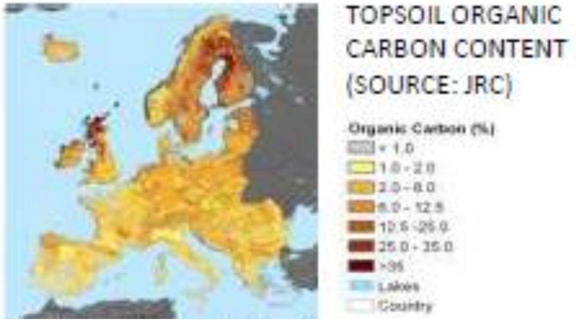
Speaking to the Guardian and four other European newspapers, the vice-president of the commission, Frans Timmermans, said Brussels' priority was to clamp down on "single-use plastics that take five seconds to produce, you use it for five minutes and it takes 500 years to break down again".

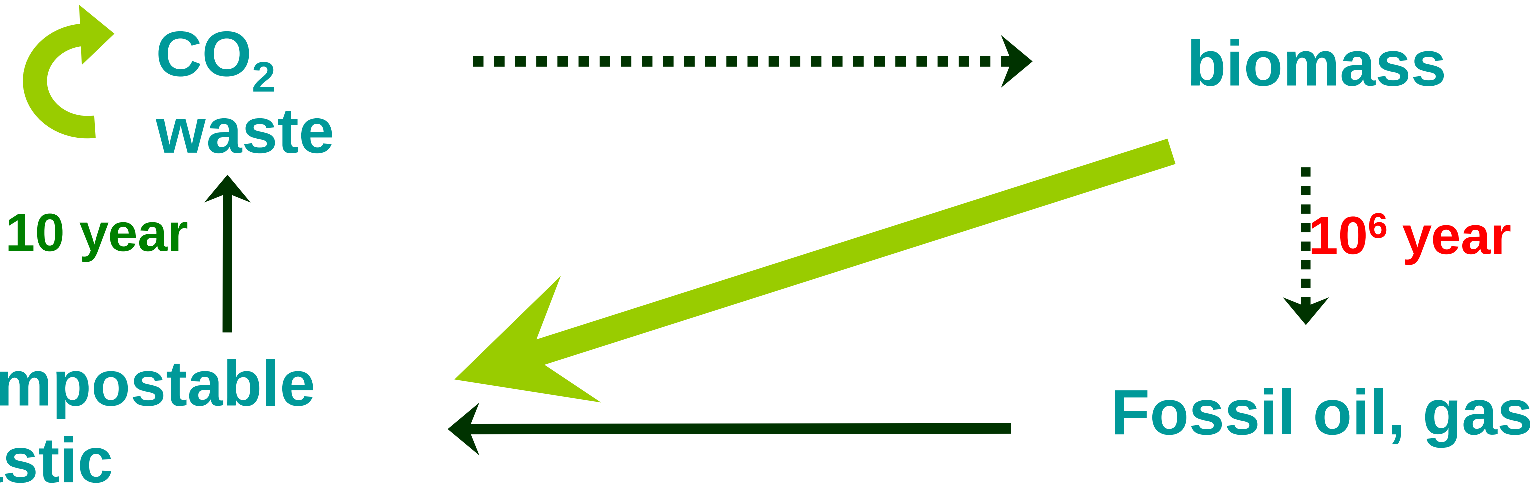
Chinese ban on plastic waste imports could see UK pollution rise
Chinese restrictions from January will hit UK recycling efforts and risk plastic waste being stockpiled or ending up in landfill, warn industry leaders.

Analysis of customs data by Greenpeace reveals British companies have shipped more than 2.7m tonnes of plastic waste to China and Hong Kong since 2012 – two-thirds of the UK's total waste plastic exports.

https://www.theguardian.com/environment/2017/dec/07/chinese-ban-on-plastic-waste-imports-could-see-uk-pollution-rise

Renewable plastics





CO_2
waste

biomass

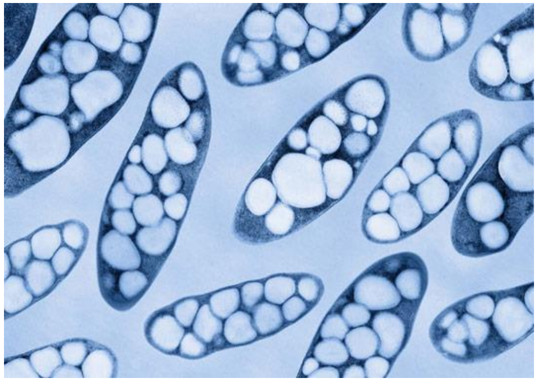
10 year

10^6 year

Compostable
plastic

Fossil oil, gas

Bio-plastics



Existing $10 billion Growing Global Market
Customers demanding renewable acrylic

Acrylic Markets %

OPXBIO Presentation for Roquette University Devel
Chemistry & Fermentation Conference - May13

8

MATER-BI

plantbottle™
up to 30% plant-based
100% recyclable bottle
redesigned plastic,
recyclable as ever.

Projections:
5.2 Billion € by 2030

Some definitions and facts

Polymers

Polymer

Organic macromolecules composed of repeating units - monomers - homogeneous raw material

Plastic (resin)

Formulated materials of which polymers are the main component

  - Thermoplastics (melt-form process) - plastics
  - Thermosets (irreversible crosslinked systems) – resins

- Very diverse group of materials

BioPolymers or bioplastics?

- **Biopolymers**: naturally occurring polymers

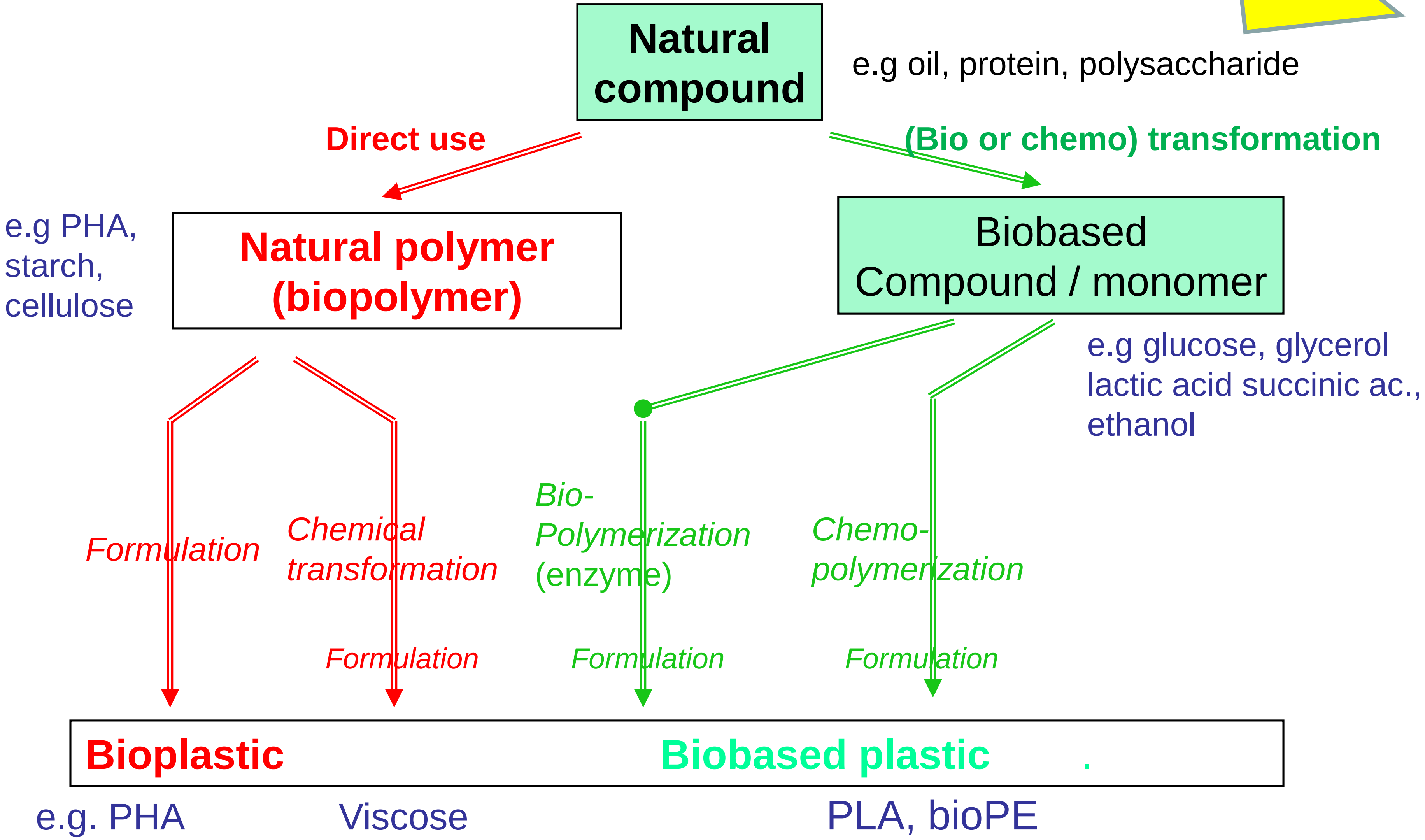
  cellulose, chitin, amylose, proteins, DNA…

- **Bioplastics**: plastics obtained by direct processing of naturally occurring polymers (biopolymers)

  thermoplastic starch, PHA, rayon

- **Biobased plastics**: plastics obtained by processing synthetic polymeric materials based on building blocks from natural feedstock PLA, nylon 11

Strategies



Natural compound

e.g oil, protein, polysaccharide

Direct use

(Bio or chemo) transformation

e.g PHA, starch, cellulose

Natural polymer (biopolymer)

Biobased Compound / monomer

e.g glucose, glycerol lactic acid succinic ac., ethanol

Formulation

Chemical transformation

Formulation

Bio-Polymerization (enzyme)

Formulation

Chemo-polymerization

Formulation

Bioplastic

Biobased plastic

e.g. PHA

Viscose

PLA, bioPE

Bio-based plastics

Not only Bio-Ethanol:
Bio-Based building blocks and monomers from biorefineries

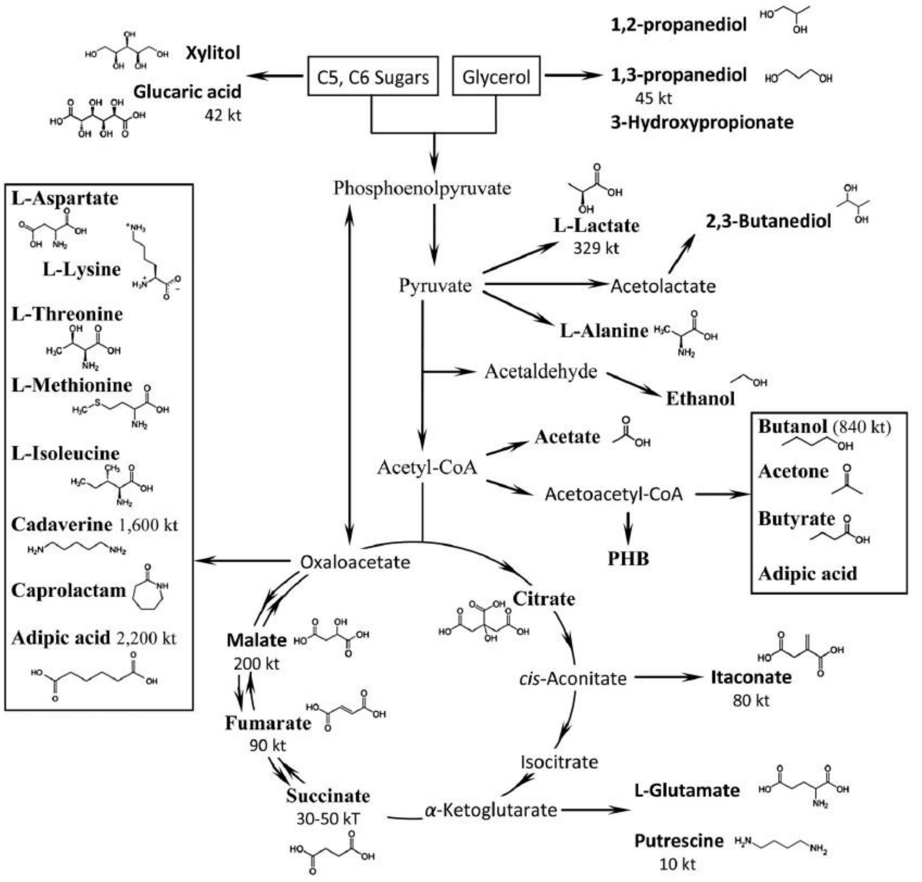
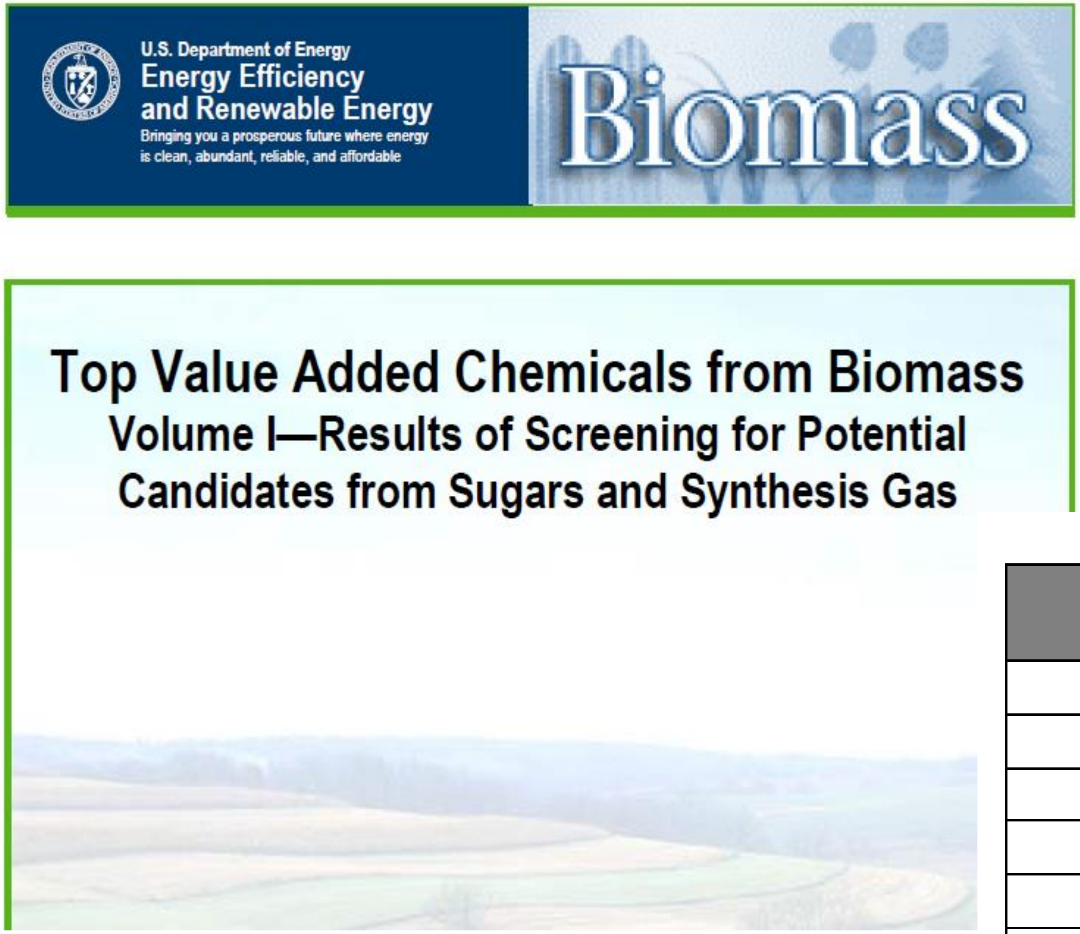


Fig. 2 Building blocks that could be produced *via* fermentation. Numbers next to biochemicals designate the total annual production in thousands of t.



U.S. Department of Energy
Energy Efficiency
and Renewable Energy
Bringing you a prosperous future where energy
is clean, abundant, reliable, and affordable

Biomass

Top Value Added Chemicals from Biomass
Volume I—Results of Screening for Potential
Candidates from Sugars and Synthesis Gas

Building Blocks
1,4 succinic, fumaric and malic acids
2,5 furan dicarboxylic acid
3 hydroxy propionic acid
aspartic acid
glucaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol/arabinitol

By 2030, the market value of bio-based building blocks is expected to reach $3.2 billion, whereas the demand for fermentation-based chemical building blocks was less than s700 million in 2013.

Such building blocks could either be produced from renewable carbon through green chemical conversion routes or via microbial conversions.

The percentage of chemical production based on biotechnology is estimated to increase from less than 2% in 2005 to approximately a quarter of all chemical production by 2025.

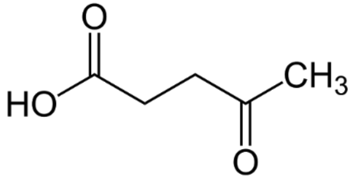
The largest contribution will come from the conversion of renewable carbon into chemicals via biotechnological routes.

The incorporation of fermentative production of basic building blocks as unit operations in integrated biorefineries is dependent on intense research activities ranging from microbial strain development and engineering to fermentation and down-stream processing optimization.

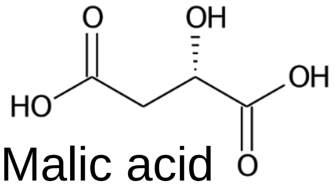
The EU demand in 2030 for biobased plastics: 5.2 BEUR

http://www.industrialbiotech-europe.eu/new/wp-content/uploads/2015/06/BIO-TIC-roadmap.pdf

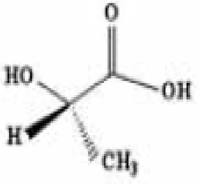
Some bio-based monomers for polymer production



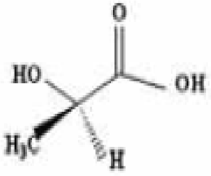
Levulinic acid



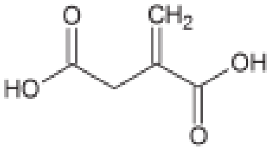
Malic acid



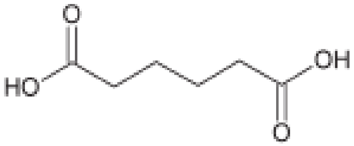
L-lactic acid



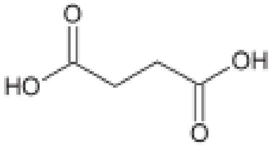
D-lactic acid



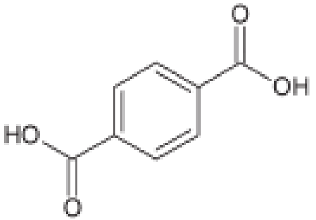
Itaconic acid (IA)



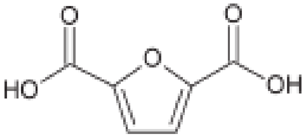
Adipic acid (AA)



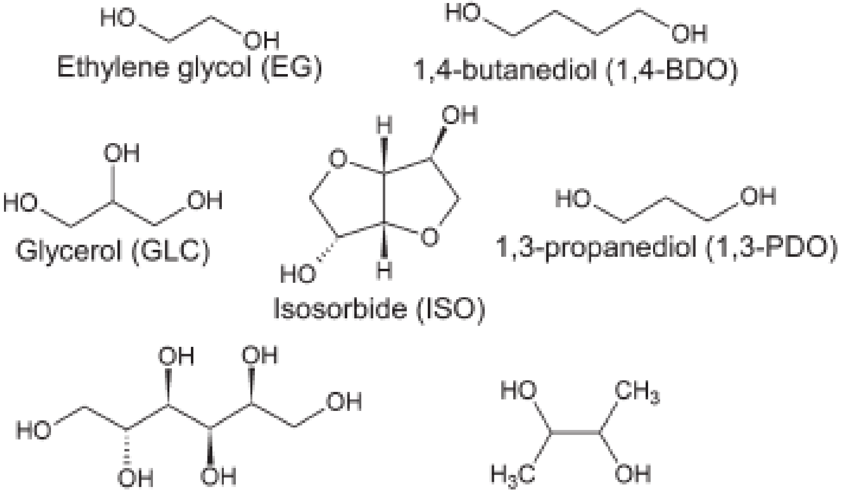
Succinic acid (SA)



Terephthalic acid (TA)



Furandicarboxylic acid (FDCA)

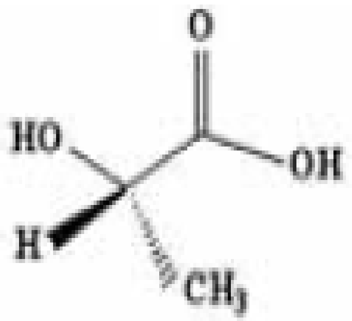


Scheme 1. Most important bio-based dicarboxylic acids and polyols currently available for the enzymatic synthesis of polyesters.

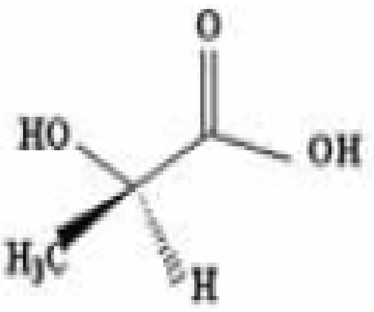
Some bio-based monomers for polymer production

Monomer	Biotechnological route		Company	Status	Application of the corresponding bio-based polyesters	.
Sorbitol	Fermentation + hydrogenation		Roquette, ADM	Market	Functional polyesters; coatings	
Isosorbide	Sorbitol dehydration		Roquette	Market	Thermosetting resins	
Ethylene glycol	Ethanol dehydration		India Glycols Ltd, Greencol Taiwan	Market	PET; PEF	
1,3-propanediol	Fermentation		Du Pont, Tate & Lyle, Metabolic Explorer	Market	PTT; fibers; elastomers; polyester-urethanes	
1,4-butanediol	Fermentation, succinic acid hydrogenation		Novamont, BioAmber, Genomatica, Mitsubishi	Market	PBAT; PBS; PBT	
Adipic acid	Fermentation + hydrogenation		Celexion LLC, BioAmber, Rennovia, Verdezyme	Market	Resins; polyester-amines; polyester-urethanes	
Itaconic acid	Fermentation		Qingdao Kehai Biochemistry, Itaconix	Market	Photocurable precursors; plasticizers	
Lactic acid	Fermentation		Nature Works, BASF, Purac, Cargill, BBCA, Galactic	Market	PLA	
Succinic acid	Fermentation		BioAmber, Myriant, Reverdia, BASF, Purac, Succinity	Market	Textiles; coatings; PBS; PBT	
Terephthalic acid	Isobutylene oxidation, fermentation		Virient, Annellotech, Genomatica	Pilot plant	PET; coatings	
Levulinic acid	Fermentation, acid treatment of C6 sugars		GFBiochemicals, Bio-on, Biofine Renewables	Market	Coatings, hyperbranched dendrimeric polyesters	
Malic acid	Fermentation		Novozymes	Pilot plant	Functionalized chiral polyesters	
2,5-furandicarboxylic acid	Fermentation + dehydration + oxidation		Avantium	Pilot plant	PEF; polyester-urethanes	

Bio-based monomers for polyesters plastics:
PLA (polylactic acid)



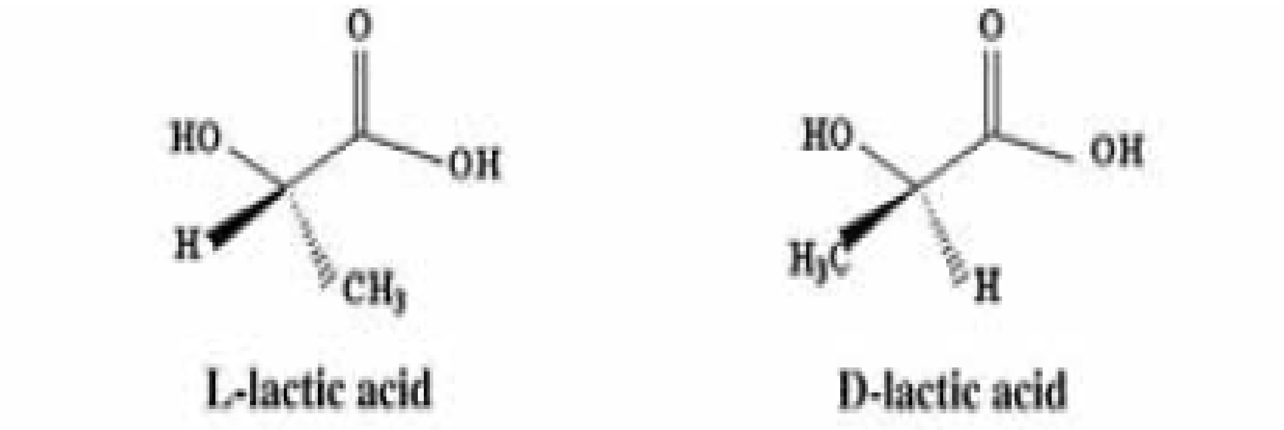
L-lactic acid



D-lactic acid

Among polymers, polyesters are a widely used class with applications ranging from clothing to food packaging and from the car industry to biomedical applications. The possibility to synthesize polyesters from bio-based monomers is demonstrated by PLA, currently the most important bio-based polyester in terms of volume, with a **capacity of approximately 180 000 tons/y.**

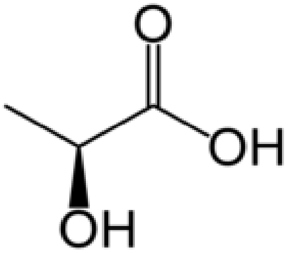
Lactic acid (2-hydroxypropionic acid), CH3–CHOHCOOH, is a simple chiral molecule which exists as two enantiomers.



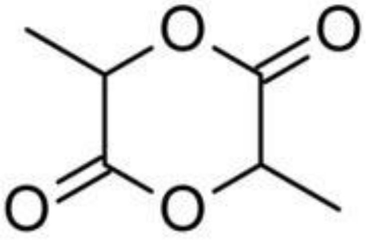
Chemical synthesis of lactic acid is mainly based on the hydrolysis of lactonitrile by strong acids, which provide only the racemic mixture of D- and L-lactic acid.

PLA was discovered in 1932 by Carothers (DuPont) who produced a low molecular weight product by heating lactic acid under vacuum. In 1954 Du Pont produced the polymer with a molecular weight greater and patented.

From lactic acid to PLA



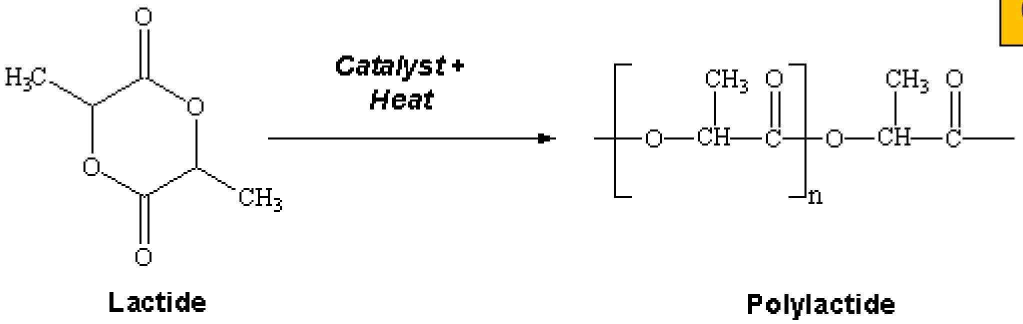
(S)-lactic acid



Lactide

Lactide is the cyclic di-ester of lactic acid, i.e., 2-hydroxypropionic acid.

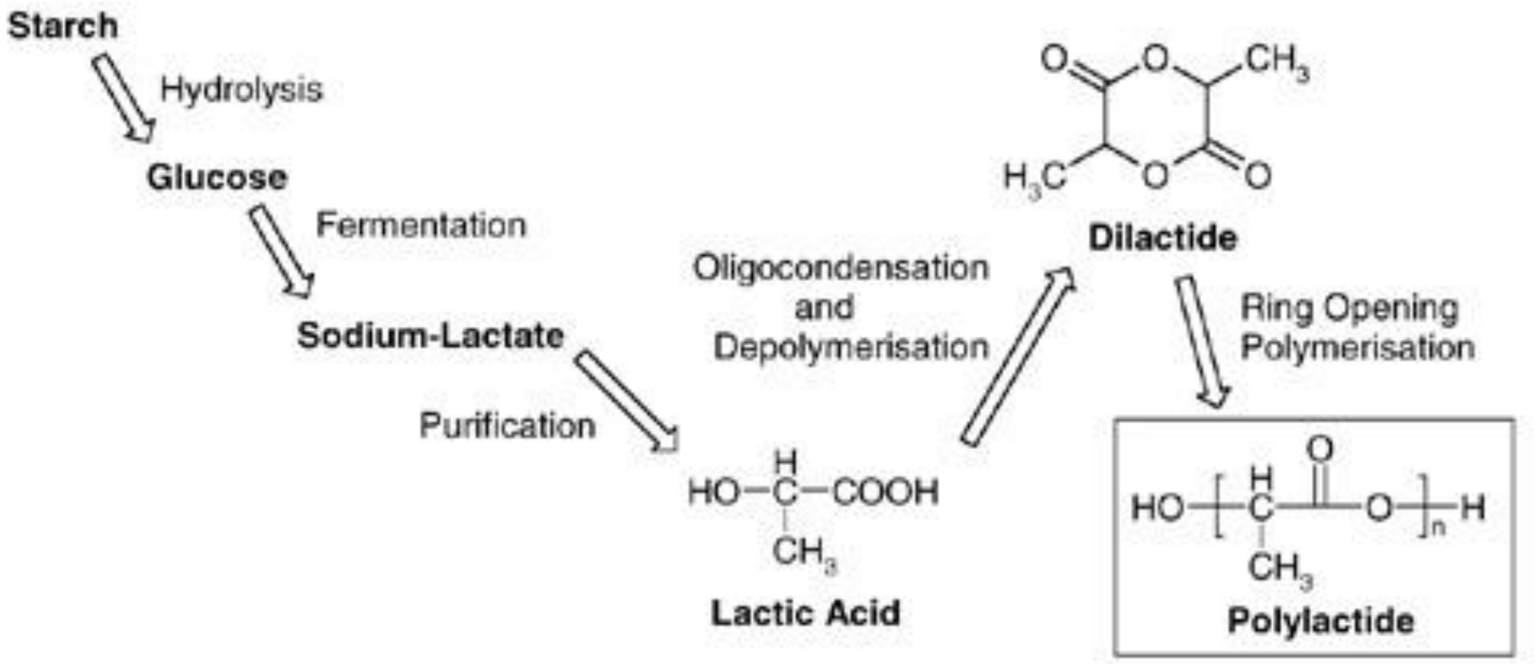
Lactic acid can not form a lactone but first forms a dimer, which contains an hydroxy group at a convenient distance from the carboxylic group for the formation of a lactone. The dimer readily forms a six-membered cyclic diester known as lactide

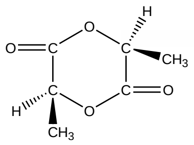


Ring opening polymerization of lactide to polylactide

- **Monomer produced in fermentation**
- **Chemical polymerization**

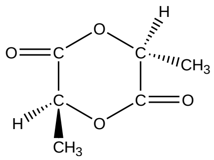
Polylactic acid





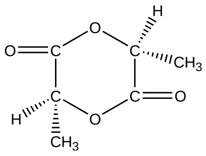
LL-Lactide

(mp 97 C)



LD-Lactide

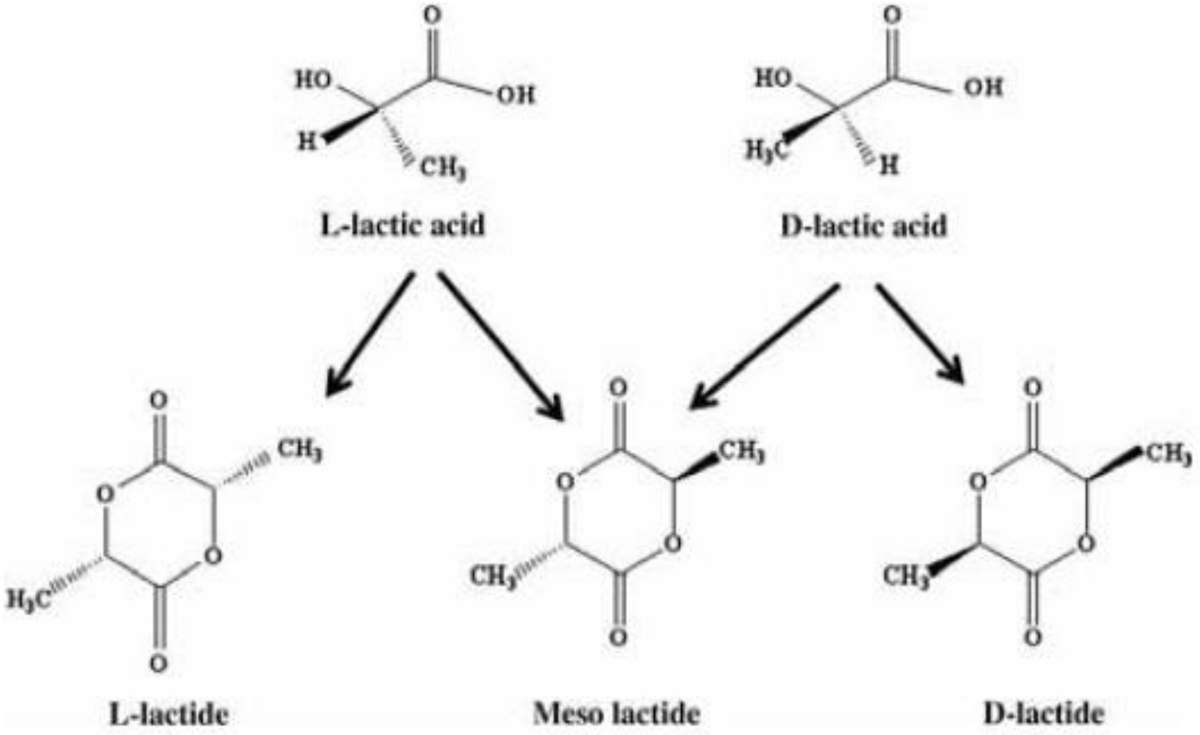
(mp 52 C)



DD-Lactide

(mp 97C)

Since, lactic acid is a chiral molecule, PLA has stereoisomers, such as poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA).



Optically active PLLA and PDLA are crystalline, whereas optically inactive PDLLA is amorphous

Companies, e.g. Cargill Dow Polymer LLC, Shimadzu Corp, Mitsui Chemicals, Musashino Co. Are now producing PLA-targeting markets for **packaging materials**, **films, textile fibers**, along with **pharmaceutical** products. The US Food and Drug Administration (FDA) and European regulatory authorities have approved the PLA resins for all food type applications and some **chirurgical** applications such as **drug releasing systems**

PLLA has gained great attention because of its excellent biocompatibility and mechanical properties. It has extensive applications in **biomedical** fields, including suture, bone fixation material, drug delivery microsphere, and tissue engineering.

However, its long degradation times coupled with the high crystallinity of its fragments can cause inflammatory reactions in the body. In order to overcome this, PLLA can be used as a material combination of L-lactic and D, L-lactic acid monomers, being the latter rapidly degraded without formation of crystalline fragments during this process.

Approximately 90% of the total lactic acid produced worldwide is made by bacterial fermentation and the remaining portion is produced synthetically by the hydrolysis of lactonitrile.

The fermentation processes to obtain lactic acid can be classified according to the type of bacteria used. The carbon source for microbial production of lactic acid can be either sugar in pure form such as glucose, sucrose, lactose or sugar containing materials such as molasses, whey, sugarcane bagasse, cassava bagasse, and starchy materials from potato, tapioca, wheat and barley. Sucrose-containing materials such as molasses are commonly exploited raw materials for lactic acid production because they represent cheaper alternatives. Sugarcane bagasse is reported to be used as support for lactic acid production by ***Rhizopus oryzae*** and ***Lactobacillus*** in solid-state fermentation by supplementing sugars or starch hydrolysates as carbon source.
More on PLA:

http://www.galateabiotech.com/it/

Besides high product specificity, as it produces a desired optically pure L-(+)- or D-(-)-lactic acid, the biotechnological production of lactic acid offers several advantages compared to chemical synthesis like low cost of substrates, low production temperature, and low energy consumption

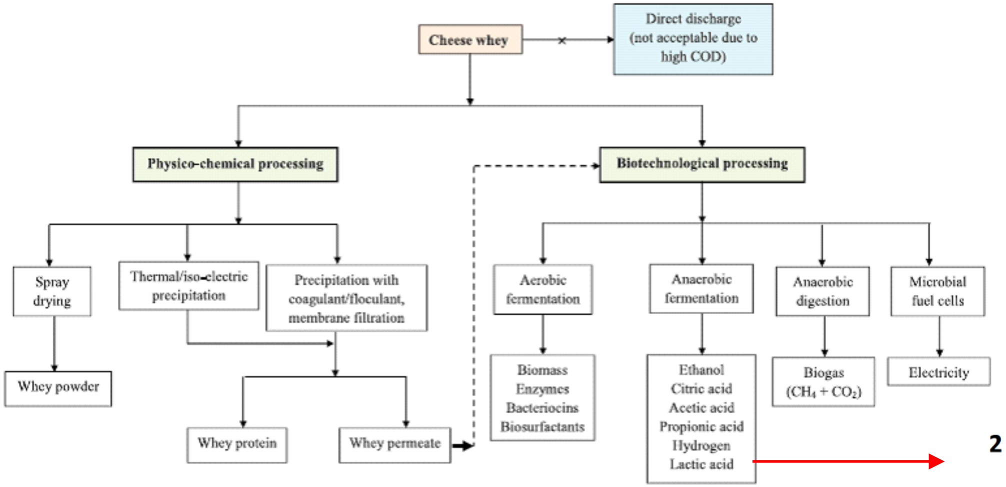
PLA-based products had already been developed by the 1940s and 1950s, but their production became economically viable only 70 years later. This demonstrates the importance of optimizing the productivity and robustness of bioconversions to achieve cost-effective production.

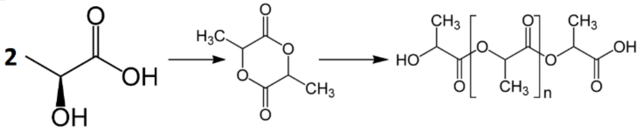
The success of bio-based polyesters does not rely solely on their capacity to replace fossil-based polymers while being economically competitive. Rather, the next generation of bio-based polyesters should bring entirely new advanced chemical and functional properties to the polymer scenario.

Waste as feedstock?

1.3 x 10^9 t of food waste generated worldwide per year

Milk whey: 180-190 M t/year

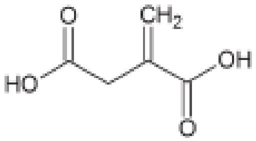




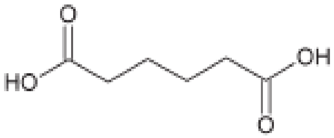
Acido lattico Lattide Acido polilattico (PLA)

cellulac U.K.

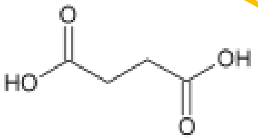
Biotecnological production of di-carboxylic acids:



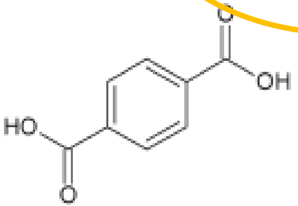
Itaconic acid (IA)



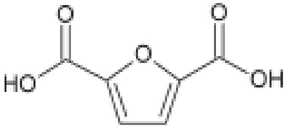
Adipic acid (AA)



Succinic acid (SA)

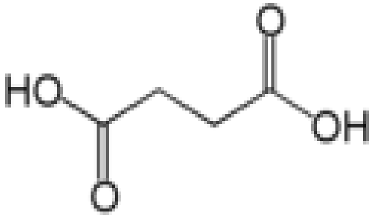


Terephthalic acid (TA)



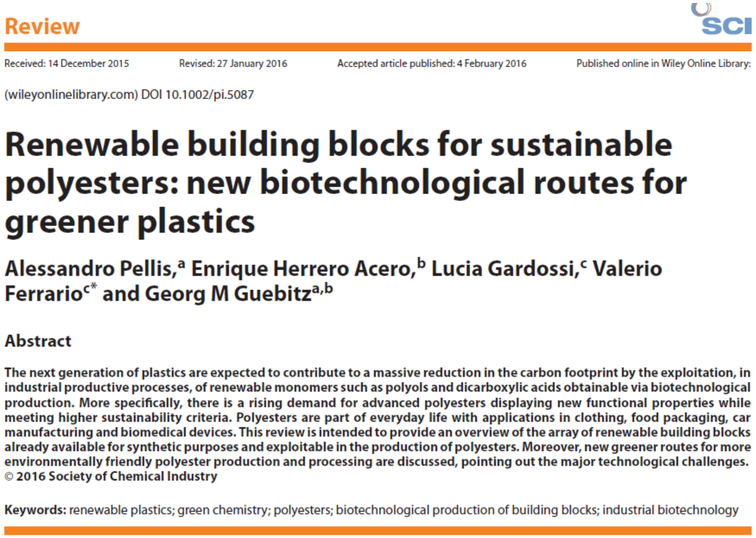
Furandicarboxylic acid (FDCA)

The high interest in SA is because of the fact that this dicarboxylic acid is a key component/intermediate in the production of several solvents, adhesives, printing inks, magnetic tapes, coating resins, plasticizers, emulsifiers, deicing compounds and chemical and pharmaceutical intermediates.



Succinic acid

Microbial strain able to convert raw hydrolysates from biomass to succinate (US Patent 6,743,610).



Review

SCI

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Renewable building blocks for sustainable polyesters: new biotechnological routes for greener plastics

Alessandro Pellis,[a] Enrique Herrero Acero,[b] Lucia Gardossi,[c] Valerio Ferrario[c*] and Georg M Guebitz[a,b]

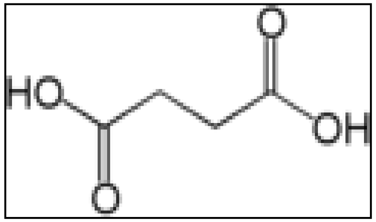
Abstract

The next generation of plastics are expected to contribute to a massive reduction in the carbon footprint by the exploitation, in industrial productive processes, of renewable monomers such as polyols and dicarboxylic acids obtainable via biotechnological production. More specifically, there is a rising demand for advanced polyesters displaying new functional properties while meeting higher sustainability criteria. Polyesters are part of everyday life with applications in clothing, food packaging, car manufacturing and biomedical devices. This review is intended to provide an overview of the array of renewable building blocks already available for synthetic purposes and exploitable in the production of polyesters. Moreover, new greener routes for more environmentally friendly polyester production and processing are discussed, pointing out the major technological challenges.

Keywords: renewable plastics; green chemistry; polyesters; biotechnological production of building blocks; industrial biotechnology

Succinic acid (SA)

Since 2008, various companies (such as DSM, BASF and Purac)
have shown an interest in the production of bio-based SA at
an industrial scale.
For SA the most important production process from renewable feedstock is microbial fermentation of various glucose sources by a variety of microorganisms such as genetically engineered microorganisms:



Escherichia coli,
Actinobacillus succiniproducens and
Anaerobiospirillum succiniproducens

The processes are in use by two companies: the Myriant SA biorefinery in Lake Providence (Louisiana, USA) that employs grain sorghum grits as its saccharificable starting material32 and the Reverdia process (used by DSM+Roquette) where ethanol and SA are co-produced through glucose fermentation.

Both processes run with genetically modified anaerobic bacteria, in such a way that alcoholic fermentation sustains the SA production.Theoretical calculations performed by Pinazo *et al.* concluded that, despite having a lower material efficiency, fermentative SA production is attracting attention due to its very competitive cost and market position close to competitiveness with an important petrochemical feedstock such as maleic anhydride.

From succinic acid (SA) to 1,4-butandiol and to adipic acid (AA)

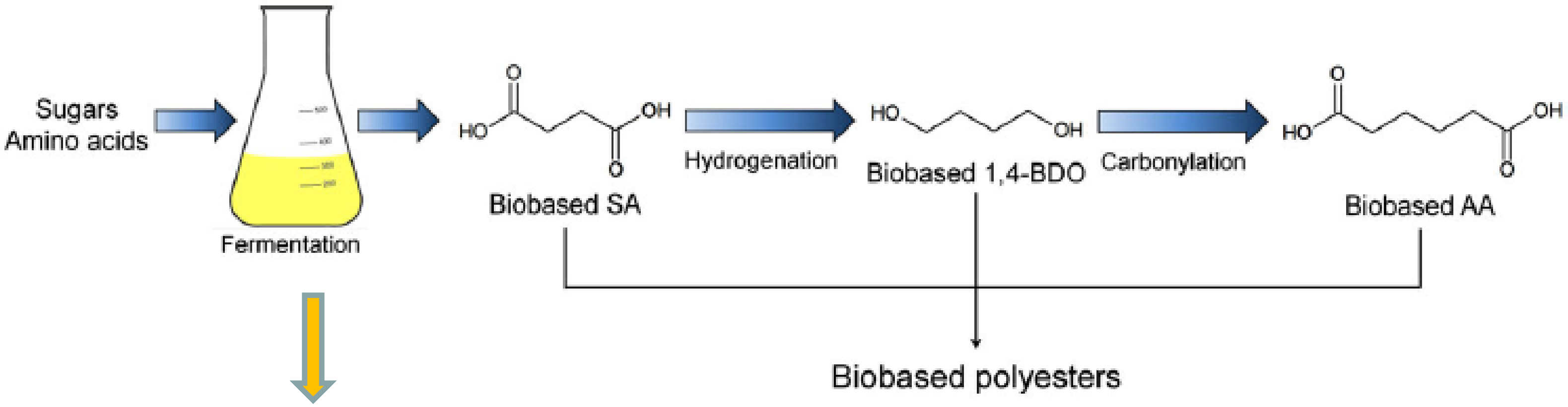
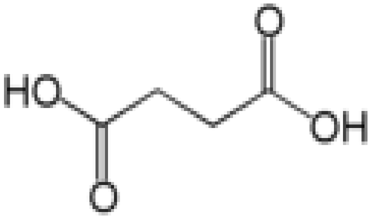
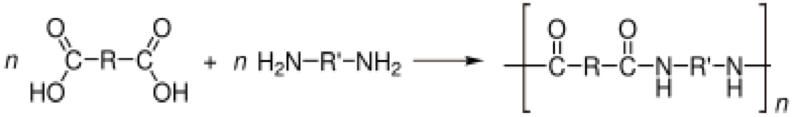


Figure 3. Biotechnological process for the production of bio-based succinic acid (SA) and its derivatives 1,4-butanediol (1,4-BDO) and adipic acid (AA).



Succinic acid

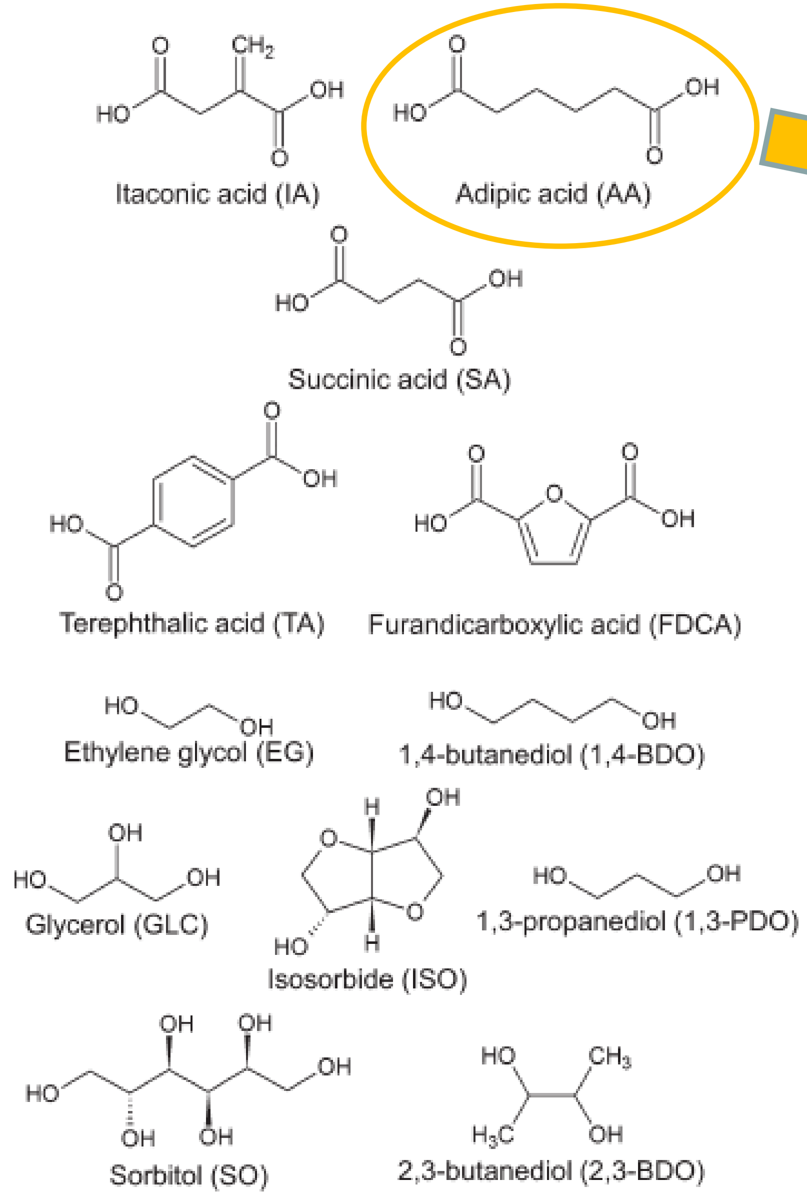


Adipic acid

nylon

Microbial strain able to convert raw hydrolysates from biomass to succinate (US Patent 6,743,610).

Biotecnological production of monomers:



Scheme 1. Most important bio-based dicarboxylic acids and polyols currently available for the enzymatic synthesis of polyesters.

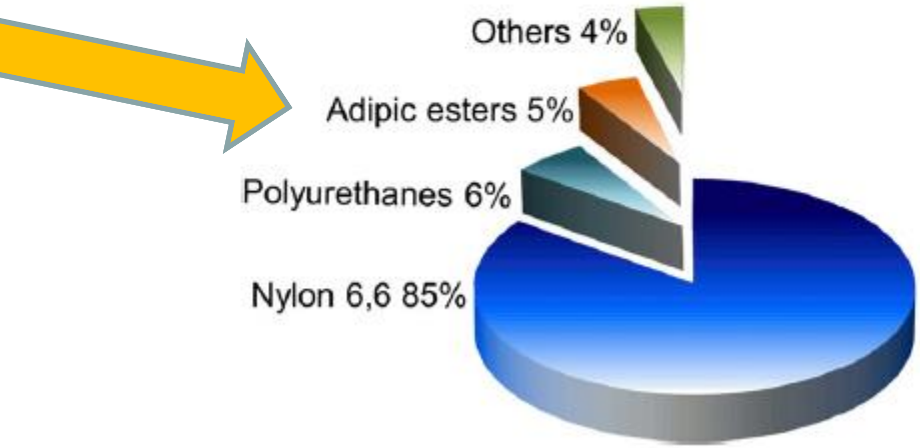
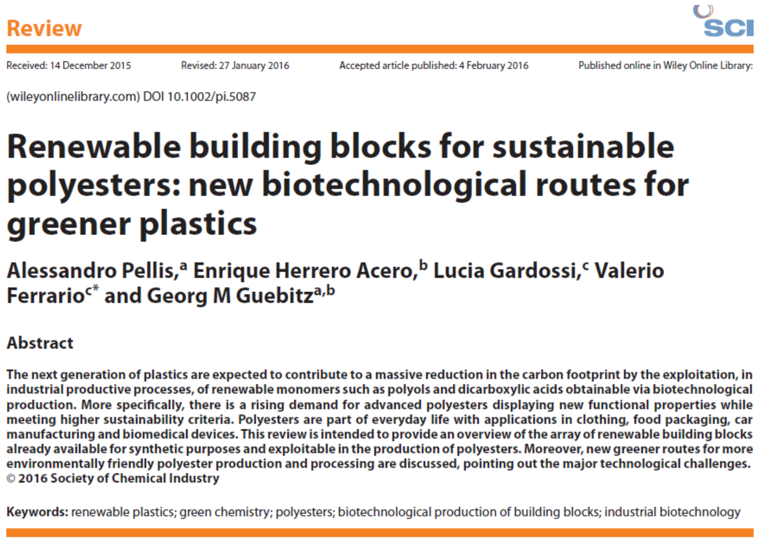


Figure 2. Most common commercial polymeric products derived from the bio-based monomer adipic acid.



Review

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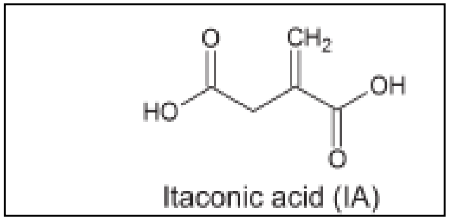
Renewable building blocks for sustainable polyesters: new biotechnological routes for greener plastics

Alessandro Pellis,[a] Enrique Herrero Acero,[b] Lucia Gardossi,[c] Valerio Ferrario[c]* and Georg M Guebitz[a,b]

Abstract

The next generation of plastics are expected to contribute to a massive reduction in the carbon footprint by the exploitation, in industrial productive processes, of renewable monomers such as polyols and dicarboxylic acids obtainable via biotechnological production. More specifically, there is a rising demand for advanced polyesters displaying new functional properties while meeting higher sustainability criteria. Polyesters are part of everyday life with applications in clothing, food packaging, car manufacturing and biomedical devices. This review is intended to provide an overview of the array of renewable building blocks already available for synthetic purposes and exploitable in the production of polyesters. Moreover, new greener routes for more environmentally friendly polyester production and processing are discussed, pointing out the major technological challenges.

Keywords: renewable plastics; green chemistry; polyesters; biotechnological production of building blocks; industrial biotechnology



Itaconic acid (IA)

IA has been known since 1837 when Baup first described the thermal decomposition of citric acid, leading to IA.

Neither thermal decomposition nor alternative chemical methods are used for commercial production since fermentation
by fungi is economically more profitable.

Biosynthesis of IA was first described by Kinoshita in 1932 who isolated the product from cultivation media of the osmophile eukaryotic *Aspergillus itaconicus*.

Various *Aspergillus terreus* strains were found more suitable for the fermentation process.

The best yields of IA production were achieved using glucose or sucrose as substrates, but for the economic sustainability of the process, complex carbon sources like starch, molasses and hydrolysates of corn syrup or wood were also tested and found to be suitable.
During the fermentation process, the pH drops below 2 and IA becomes the main fermentation product.

Economically speaking, the most productive process was established by Pfizer which involves a submerged fermentation process using suspended *A. terreus* biomass, inoculated as spores on pretreated molasses.

IA is currently used in paper-coating and carpet-backing, which are the primary consumers at the industrial scale. Some IA derivatives are used in medicines, cosmetics, lubricants and herbicides.

Polyols obtained by fermentations

Some bio-based monomers for polymer production

Monomer	Biotechnological route		Company	Status	Application of the corresponding bio-based polyesters	.
Sorbitol	Fermentation + hydrogenation		Roquette, ADM	Market	Functional polyesters; coatings	
Isosorbide	Sorbitol dehydration		Roquette	Market	Thermosetting resins	
Ethylene glycol	Ethanol dehydration		India Glycols Ltd, Greencol Taiwan	Market	PET; PEF	
1,3-propanediol	Fermentation		Du Pont, Tate & Lyle, Metabolic Explorer	Market	PTT; fibers; elastomers; polyester-urethanes	
1,4-butanediol	Fermentation, succinic acid hydrogenation		Novamont, BioAmber, Genomatica, Mitsubishi	Market	PBAT; PBS; PBT	
Adipic acid	Fermentation + hydrogenation		Celexion LLC, BioAmber, Rennovia, Verdezyme	Market	Resins; polyester-amines; polyester-urethanes	
Itaconic acid	Fermentation		Qingdao Kehai Biochemistry, Itaconix	Market	Photocurable precursors; plasticizers	
Lactic acid	Fermentation		Nature Works, BASF, Purac, Cargill, BBCA, Galactic	Market	PLA	
Succinic acid	Fermentation		BioAmber, Myriant, Reverdia, BASF, Purac, Succinity	Market	Textiles; coatings; PBS; PBT	
Terephthalic acid	Isobutylene oxidation, fermentation		Virient, Annellotech, Genomatica	Pilot plant	PET; coatings	
Levulinic acid	Fermentation, acid treatment of C6 sugars		GFBiochemicals, Bio-on, Biofine Renewables	Market	Coatings, hyperbranched dendrimeric polyesters	
Malic acid	Fermentation		Novozymes	Pilot plant	Functionalized chiral polyesters	
2,5-furandicarboxylic acid	Fermentation + dehydration + oxidation		Avantium	Pilot plant	PEF; polyester-urethanes	

1,4-Butanediol (1,4-BDO)

1,4-BDO is an important chemical that is used for the manufacture of over 2.5 million tons of polymers annually. Nowadays its production is almost entirely based on fossil carbon resources (production via the Reppe process in which acetylene is reacted with formaldehyde) with the exception of BASF and Bioamber that started production via hydrogenation of SA which is accessible from biogenic sources as described below.

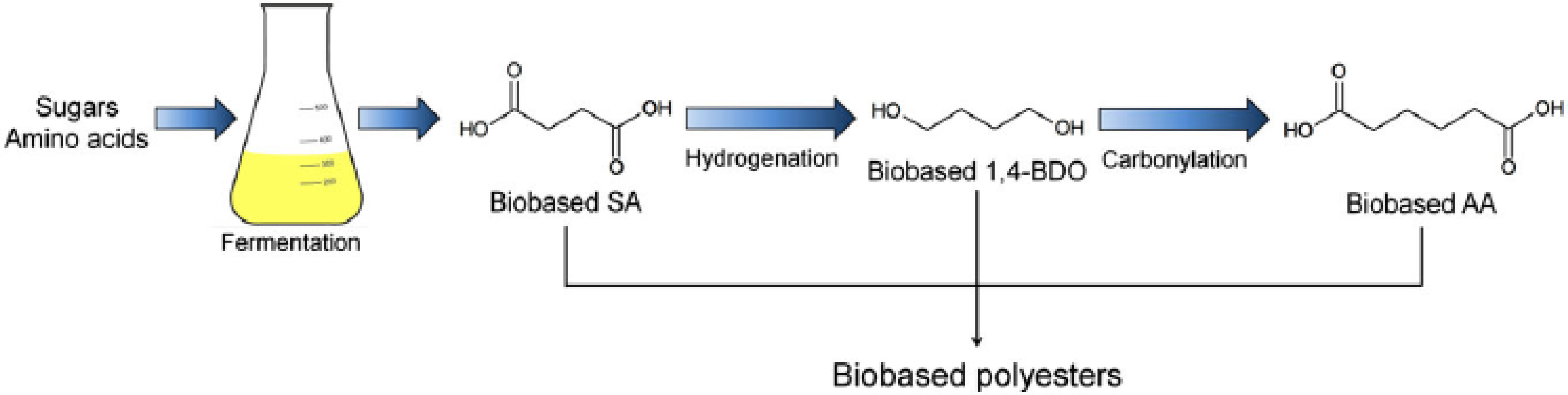
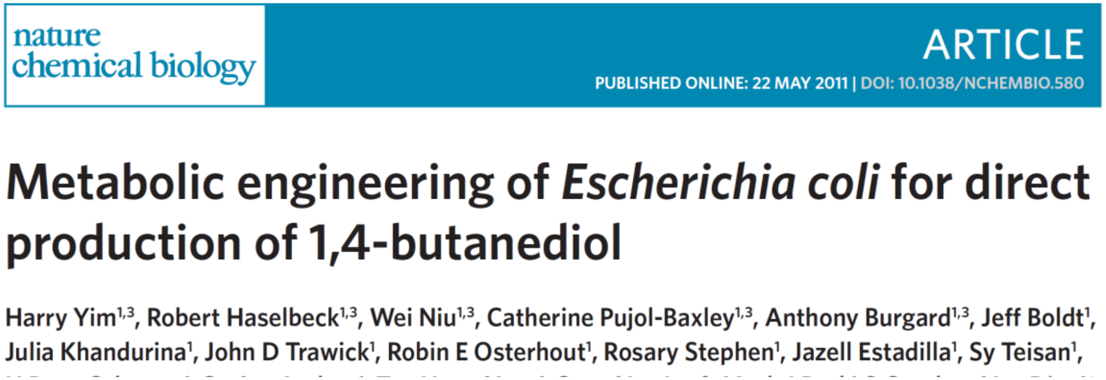


Figure 3. Biotechnological process for the production of bio-based succinic acid (SA) and its derivatives 1,4-butanediol (1,4-BDO) and adipic acid (AA).

In September 2016 Novamont opened the first plant at commercial scale in the world for the direct fermentation of sugar to produce 1,4-butandiol.



nature chemical biology

ARTICLE

PUBLISHED ONLINE: 22 MAY 2011 | DOI: 10.1038/NCHEMBIO.580

Metabolic engineering of *Escherichia coli* for direct production of 1,4-butanediol

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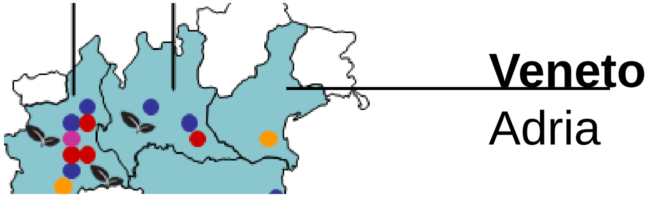

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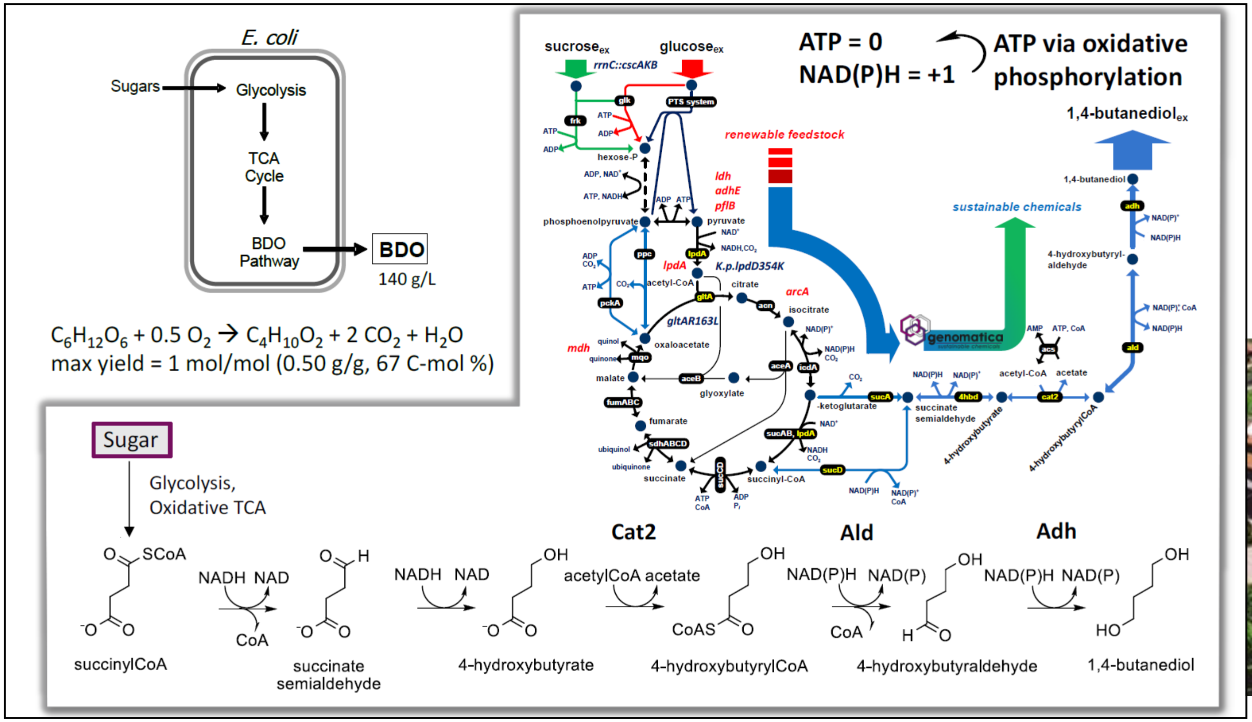
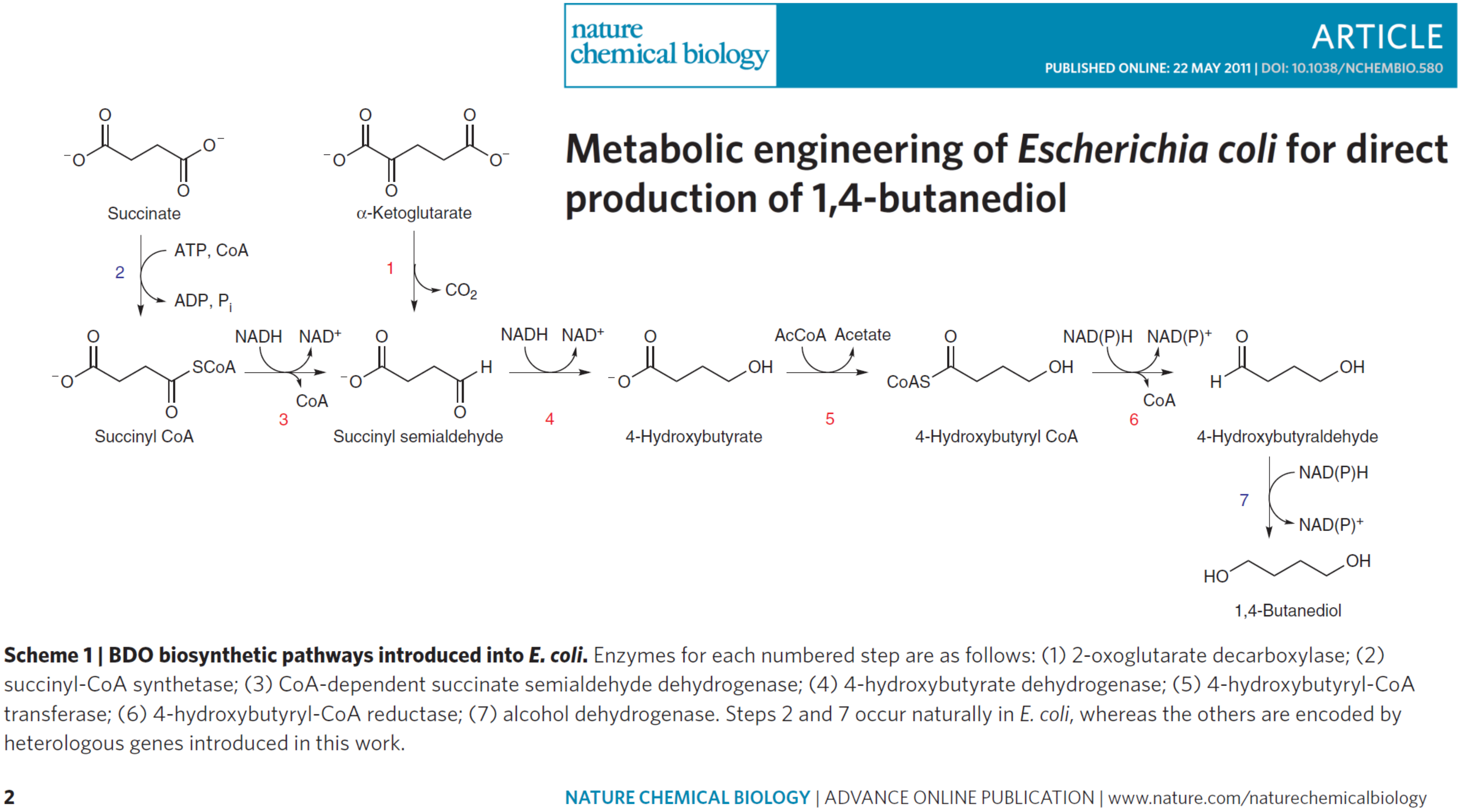


$C_6H_{12}O_6 + 0.5\ O_2 \rightarrow C_4H_{10}O_2 + 2\ CO_2 + H_2O$

max yield = 1 mol/mol (0.50 g/g, 67 C-mol %)

In September 2016 Novamont opened the first plant at commercial scale in the world for the direct fermentation of sugar to produce 1,4-butandiol.



nature chemical biology

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Scheme 1 | BDO biosynthetic pathways introduced into *E. coli*. Enzymes for each numbered step are as follows: (1) 2-oxoglutarate decarboxylase; (2) succinyl-CoA synthetase; (3) CoA-dependent succinate semialdehyde dehydrogenase; (4) 4-hydroxybutyrate dehydrogenase; (5) 4-hydroxybutyryl-CoA transferase; (6) 4-hydroxybutyryl-CoA reductase; (7) alcohol dehydrogenase. Steps 2 and 7 occur naturally in *E. coli*, whereas the others are encoded by heterologous genes introduced in this work.

2 NATURE CHEMICAL BIOLOGY | ADVANCE ONLINE PUBLICATION | www.nature.com/naturechemicalbiology

1,4-BDO **derivatives:**

- tetrahydrofuran
- γ-butyrolactone
- *N*-methylpyrrolidone
- 2-pyrrolidone

1,4-BDO is an important chemical that is used for the manufacture of over 2.5 million tons of polymers annually1,4-BDO and its derivatives represent a market ripe for the introduction of a competitive bio-based route

nature chemical biology

ARTICLE

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[1]Genomatica, Inc., San Diego, California, USA. [2]Department of Chemical and Biomolecular Engineering (BK21 program), Center for Systems and Synthetic Biotechnology, Institute for the BioCentury, Korea Advanced Institute of Science and Technology, Daejeon, South Korea. [3]These authors contributed equally to this work. *e-mail: svandien@genomatica.com

1,4-Butanediol (BDO) is an important commodity chemical used to manufacture over 2.5 million tons annually of valuable polymers, and it is currently produced exclusively through feedstocks derived from oil and natural gas. Herein we report what are to our knowledge the first direct biocatalytic routes to BDO from renewable carbohydrate feedstocks, leading to a strain of *Escherichia coli* capable of producing 18 g l^{-1} of this highly reduced, non-natural chemical. A pathway-identification algorithm elucidated multiple pathways for the biosynthesis of BDO from common metabolic intermediates. Guided by a genome-scale metabolic model, we engineered the *E. coli* host to enhance anaerobic operation of the oxidative tricarboxylic acid cycle, thereby generating reducing power to drive the BDO pathway. The organism produced BDO from glucose, xylose, sucrose and biomass-derived mixed sugar streams. This work demonstrates a systems-based metabolic engineering approach to strain design and development that can enable new bioprocesses for commodity chemicals that are not naturally produced by living cells.

Thanks to an investment of 100 million euro, Novamont has managed to revive an abandoned manufactory site of Bioitalia, former Ajinomoto, who was acquired in 2012 by Novamont, safeguarding 27 jobs, which later became 51 at the end of 2015.
The plant of Bottrighe di Adria is the first facility in the world capable of producing butanediol (BDO) directly from sugars (30 thousand tons yearly).

BDO produced by the plant enables Novamont to deliver its fourth-generation of Mater-Bi bioplastics with greater sustainability (e.g. renewable components).

The products made with this new BDO will save an estimated 56 percent of greenhouse gas emissions compared to the use of conventional BDO.

CONFERENZA
INTERNAZIONALE

RICONNETTERE
ECONOMIA E SOCIETÀ
ATTRAVERSO L'INNOVAZIONE

Una nuova
infrastruttura della bioeconomia
per la rigenerazione territoriale

30 settembre 2016
Museo Regionale della Bonifica
Taglio di Po, Rovigo, Italy

https://www.youtube.com/watch?v=cWPcKil4z4M

https://www.youtube.com/watch?v=awxsW2nzsN8


ATTENZIONE

Chemical platform for 3-hydroxypropionic acid

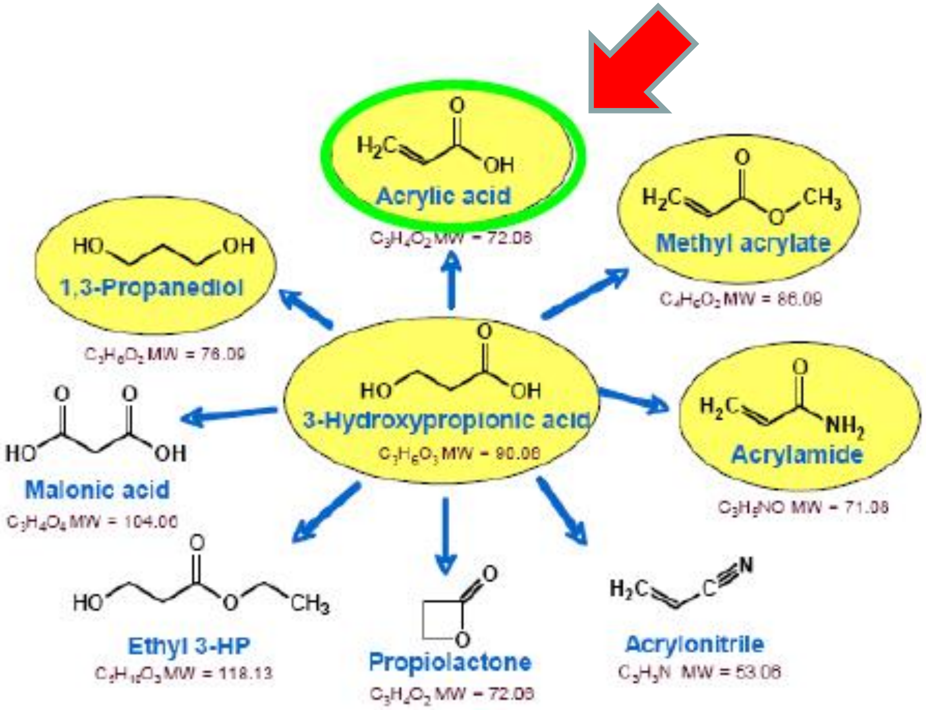
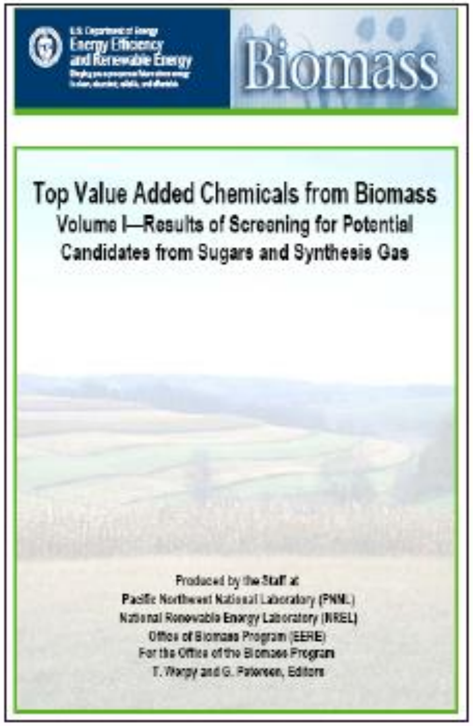


Figure 8 – Derivatives of 3-HPA



U.S. Department of Energy
Energy Efficiency and Renewable Energy

Biomass

Top Value Added Chemicals from Biomass
Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas

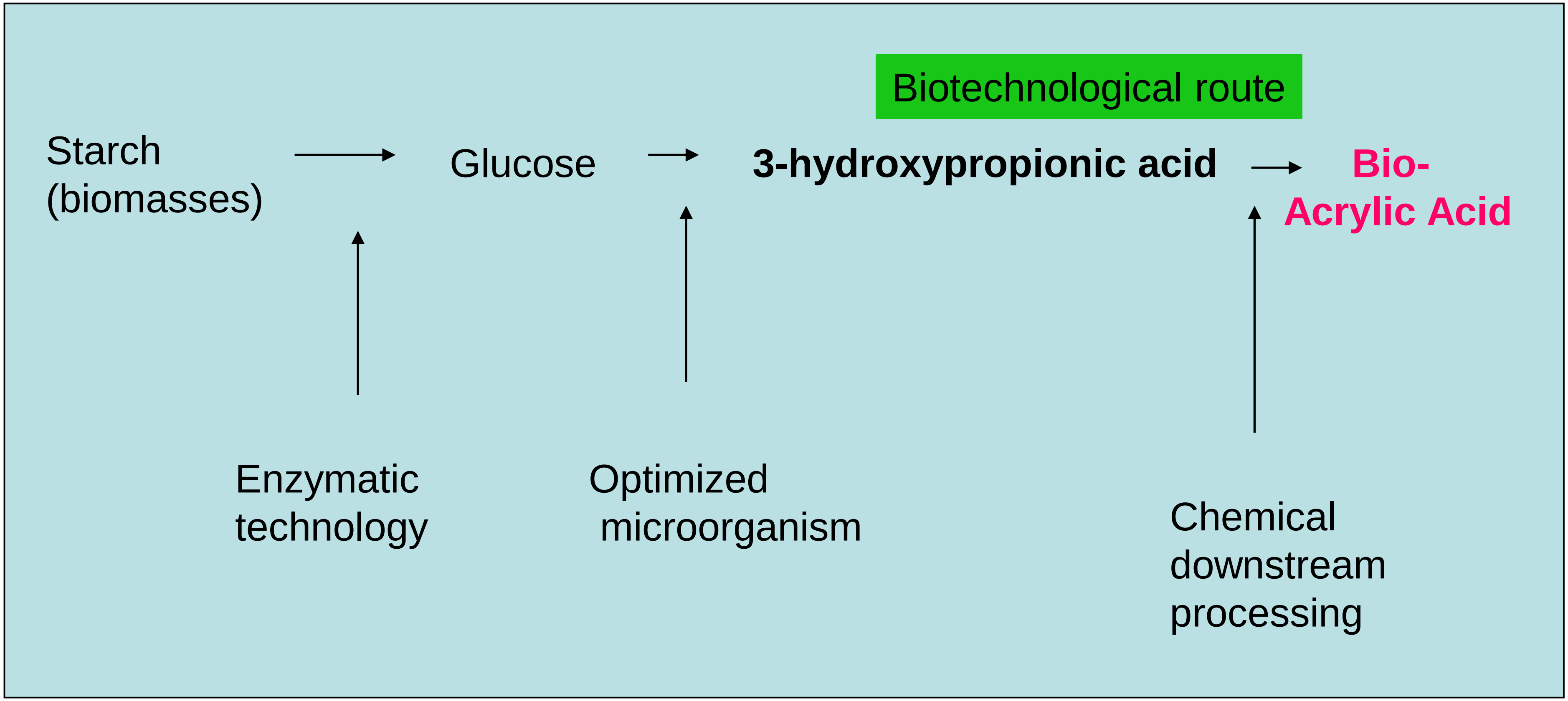
Produced by the Staff at
Pacific Northwest National Laboratory (PNNL)
National Renewable Energy Laboratory (NREL)
Office of Biomass Program (EERE)
For the Office of the Biomass Program
T. Werpy and G. Petersen, Editors

http://www1.eere.energy.gov/biomass/pdfs/35523.pdf

Production of Bio-acrylic acid

Propylene → Acrylic acid

Chemical route



Biotechnological route

Starch (biomasses) → Glucose → **3-hydroxypropionic acid** → **Bio-Acrylic Acid**

Enzymatic technology

Optimized microorganism

Chemical downstream processing

(source Novozymes communication)

1,3-Propanediol (1,3-PDO)

The microbial production of 1,3-PDO is one of the oldest processes reported in the literature.

This diol has a wide range of possible applications, e.g. composites, adhesives, solvents, monomers for aliphatic polyesters, and as an anti-freezing agent. In addition, 1,3-PDO is used for the production of **poly(trimethylene terephthalate),** a polymer with remarkable ‘stretch–recovery’ properties that is used in specialty resins and other applications.

Various bacteria including *Klebsiella pneumoniae*, *Enterobacter agglomerans*, *Lactobacillus brevis* and *Clostridium butyricum* have been reported to produce 1,3-PDO during anaerobic growth on glycerol.45 The highest concentration of 1,3-PDO was obtained using a *K. pneumonia* strain that led to a concentration of 73.3 g L−1.

Bio-Polyethylene

- Equivalent to fossil based PE
- 100 % biobased (ASTM 6866)
- Not biodegradable
- Braskem 2009, 200.000 t/a
- Dow 2011, 350,000 t/a
- Solvay PVC

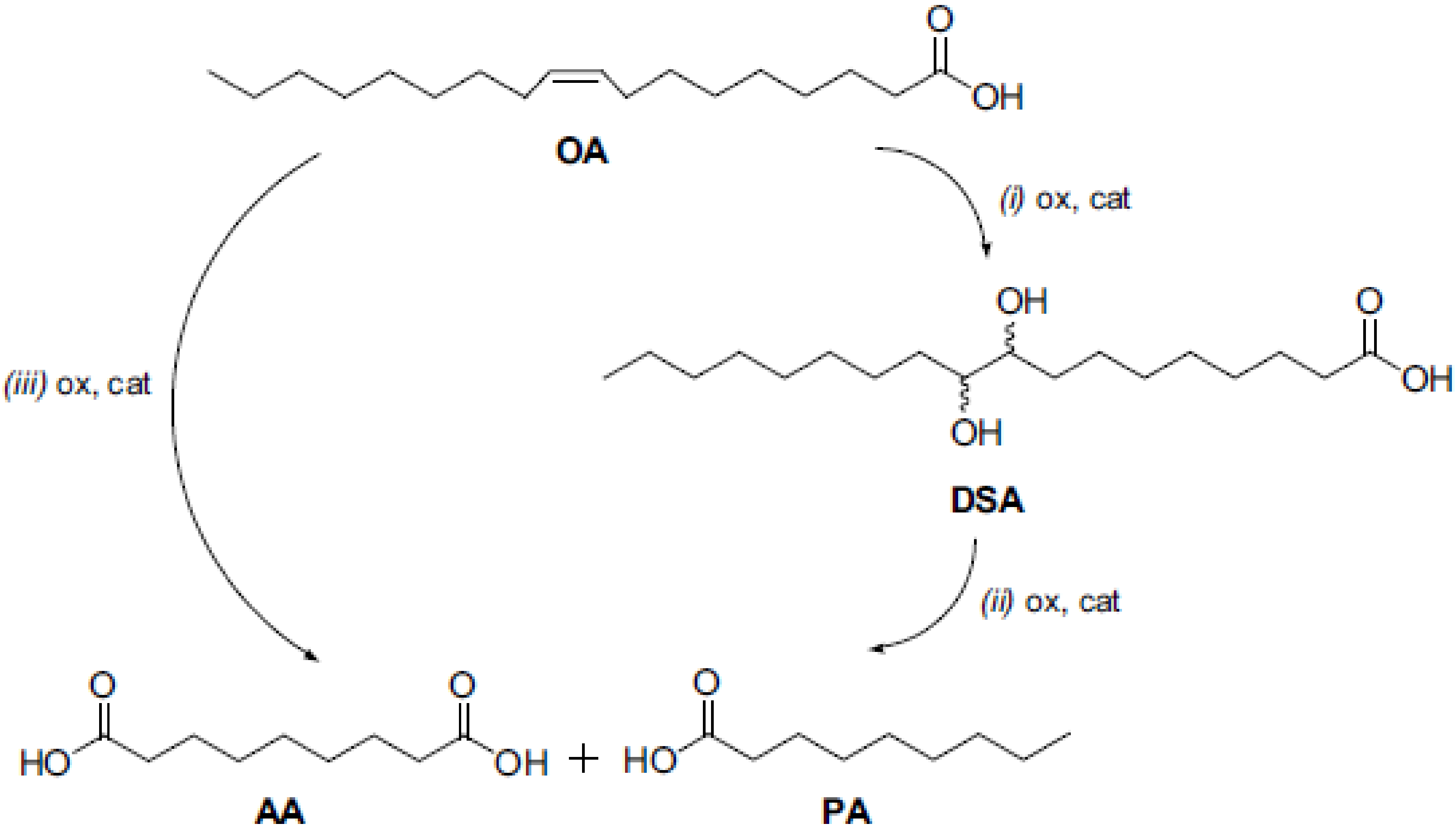
Sugar Cane
↓ fermentation, distillation
Ethanol
↓ chemical dehydration
Ethylene
↓ polymerization
PE

- Ethanol fermentation carbon efficiency?

$$C_6H_{12}O_{6(l)} + H_2O_{(l)} \rightarrow 2C_2H_5OH_{(l)} + 2CO_{2(g)} + H_2O_{(l)} + heat$$

Bio-based monomers and building blocks obtained by chemical routes

Synthesis of azelaic acid and pelargonic acid from oleic acid



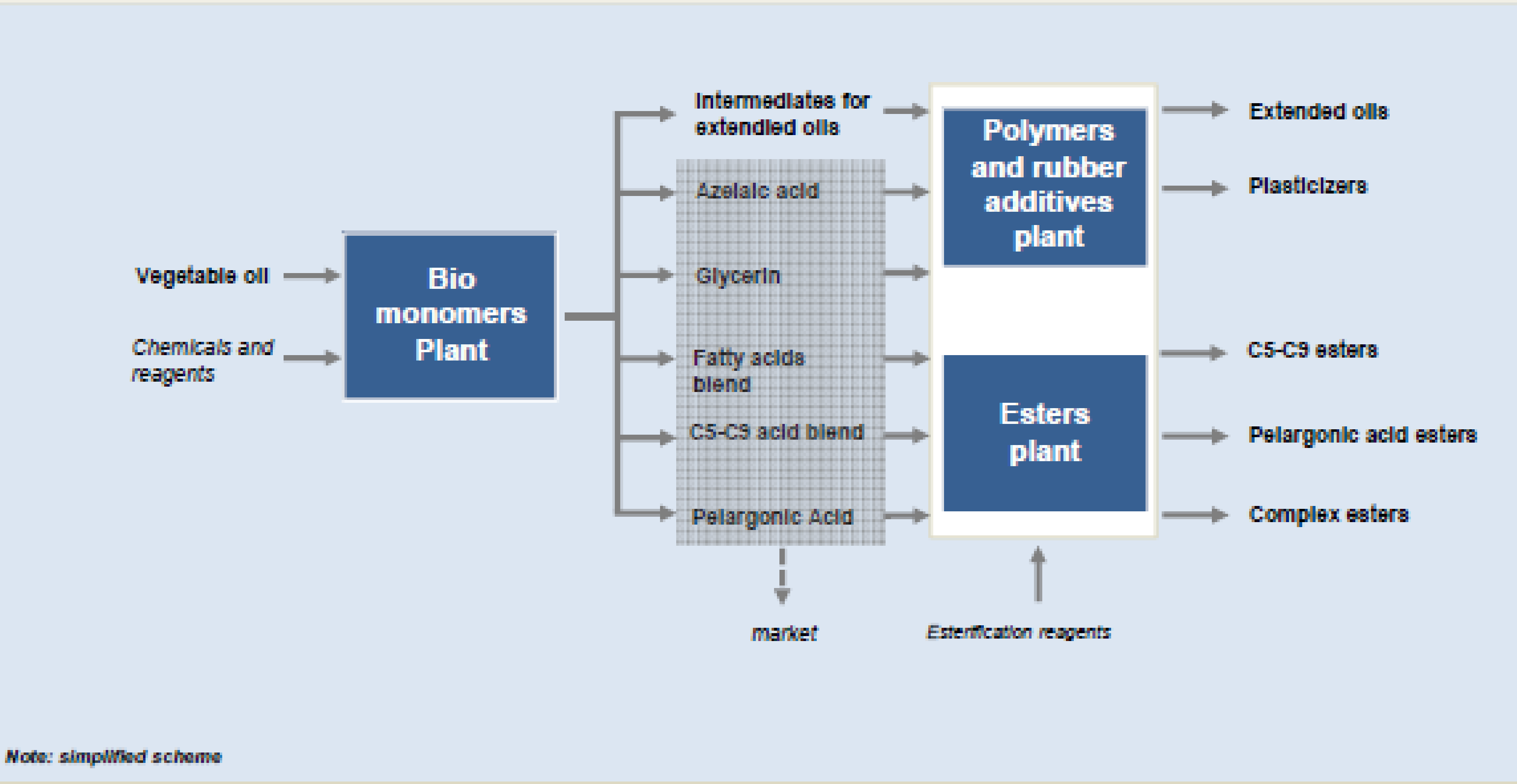
Crops from marginal lands

Porto Torres: From a traditional petrochemical site to a biorefinery

Matrica

eni versalis

Novamont
Chimica Vivente per la Qualità della Vita.



Vegetable oil

Chemicals and reagents

Bio monomers Plant

Intermediates for extended oils

Azelaic acid

Glycerin

Fatty acids blend

C5-C9 acid blend

Pelargonic Acid

market

Polymers and rubber additives plant

Esters plant

Esterification reagents

Extended oils

Plasticizers

C5-C9 esters

Pelargonic acid esters

Complex esters

Note: simplified scheme

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Sectors where Matrica Products will Contribute to the Quality of Environment

	PLASTICIZERS FOR PVC AND OTHER POLYMERS AS REPLACEMENT OF PHTALATES	**WORLDWIDE PRODUCTION OF PHTALATES: 5,5 MIO TON**
	BIOLUBRICANTS FOR AGRICULTURE, MARINE AND INDUSTRIAL APPLICATIONS: high lubricity, biodegradability, low flammability	**EU PRODUCTION OF LUBRICANTS: 5,2 MIO TON** **HYDRAULICFLUIDS: 0,7 MIO TON**
	PALM OIL FREE COMPONENTS FOR COSMETICS	
	OIL EXTENDERS FOR RUBBER	**EUROPEAN PRODUCTION: > 0,5MIO TON**
	BIO-HERBICIDES FOR INTEGRATED AGRICULTURE	

Novamont

Luigi Capuzzi
luigi.capuzzi@novamont.com

What crops for Sardinia? : An example : Thistle (Cynara Cardunculus)

- ✓ It is a spontaneous polyennial plant
- ✓ It needs amount of water compatible with winter rain regime (400 mm)
- ✓ It can be grown in marginal areas become a source of extra income for farmers and sheperds
- ✓ It produces oil usable as feedstock for the monomers plant
- ✓ Proteic meals can be used in feed

- ✓ It produces big amount of biomass usable immediately to produce all the energy needed by the plant and in the mid term for the manufacturing of strategic monomers

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Some images from thistle harvesting in Matrìca experimental fields (August 2014)

AFTER 3 CONSECUTIVE YEARS OF EXPERIMENTATION:

- BIOMASS PRODUCTION > 15 TON/HA (17 TON/HA IN 2014)
- SEEDS PRODUCTION ~ 1,5 TON/HA (1,74 TON/HA IN 2014)
- ENGINEERING OF SPECIFIC FARMING MACHINES SUITABLE FOR SARDINIAN STONY GROUNDS

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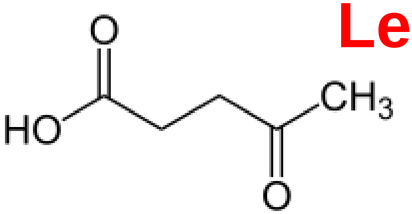
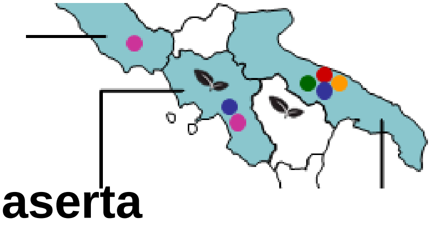
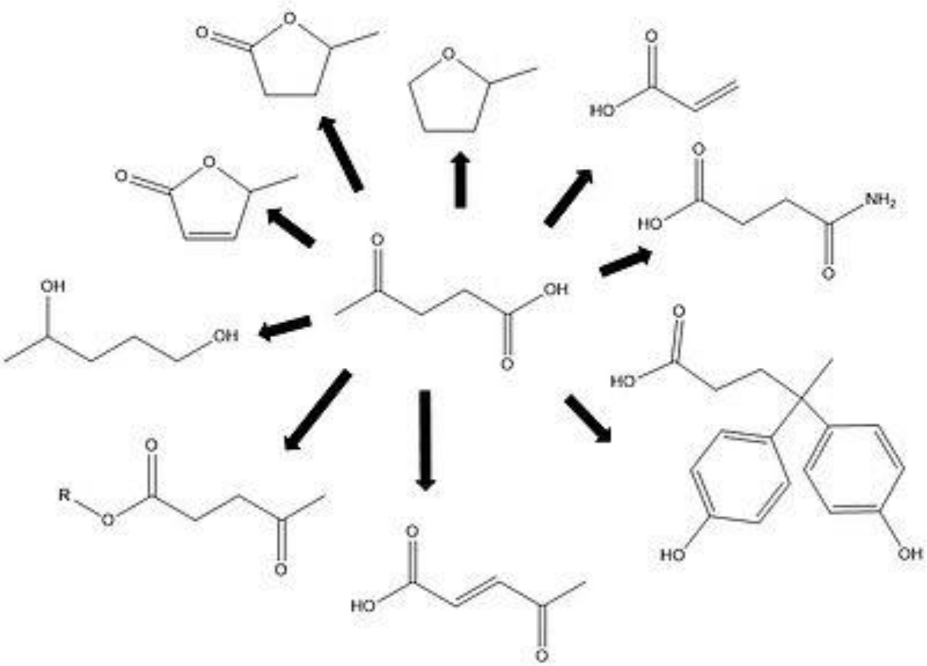
Levulinic acid platform



Levulinic acid



Process developed with the Univ. of Pisa: thermochemical conversion of carbohydrates.
Biomass pre-treatment includes acid hydrolysis for the conversion into C5 and C6 sugars.



pharmaceuticals
agrochemicals
flavours
fragrances
food additives
resins

coatings,
plasticisers
solvents,
fuel additives
biofuels

GFBiochemicals

FIRST COMPANY TO PRODUCE LEVULINIC ACID DIRECTLY FROM BIOMASS AT COMMERCIAL SCALE

Basics:

- > Proprietary technology portfolio
- > Production assets - Start-up phase
- > Experienced R&D, Engineering & Commercial team
- > Pilot plant and application laboratories

- > Established : 2008
- > Employees : 50

Our Mission:
Bringing levulinic acid to the market by technology innovation

Our locations:

Pilot plant and application lab
Minneapolis, USA

R&D and Marketing & Sales
Geleen, the Netherlands

Headquarters
Milan, Italy

10,000 MT/a levulinic acid plant
Caserta, Italy

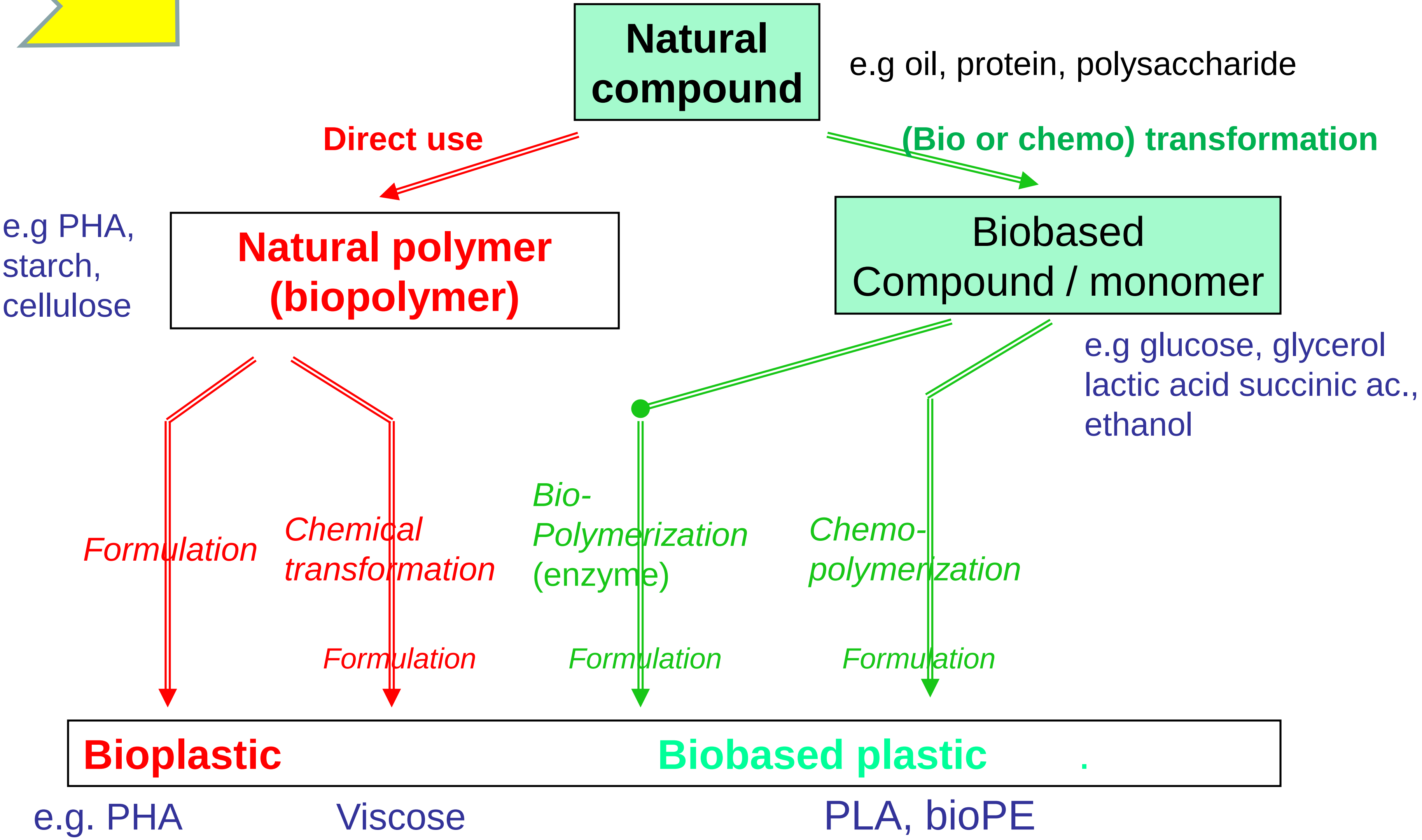
GF Biochemicals

In 2016 GF Biochemicals acquired
the American company Segetis

07.04.2017
Italian levulinic acid producer GF Biochemicals and American Process Inc. (API), a **bioprocess** technology firm, have announced plans to jointly build a **cellulosic** biorefinery in the U.S.

Bioplastics

Strategies



Natural compound

e.g oil, protein, polysaccharide

Direct use

(Bio or chemo) transformation

e.g PHA, starch, cellulose

Natural polymer (biopolymer)

Biobased Compound / monomer

e.g glucose, glycerol lactic acid succinic ac., ethanol

Formulation

Chemical transformation

Bio-Polymerization (enzyme)

Chemo-polymerization

Formulation

Formulation

Formulation

Bioplastic

Biobased plastic .

e.g. PHA

Viscose

PLA, bioPE

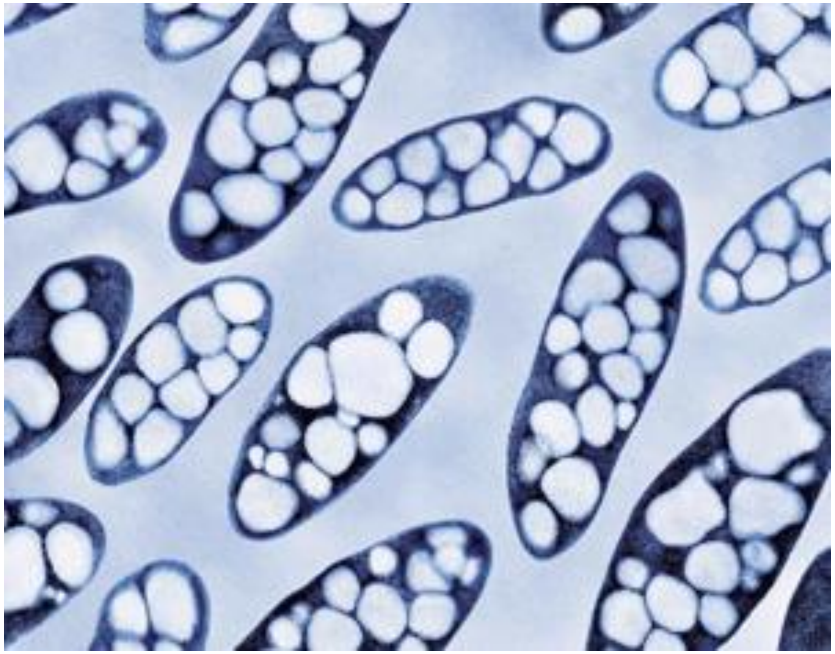
Polyhydroxyalcanoates (PHA)

- Polyester (thermoplastic) produced by microorganisms in response to conditions of physiological stress
- Represent a form of energy storage molecule to be metabolized when other common energy sources are not available

Current production based on sucrose, glucose

Established methodology using waste sources

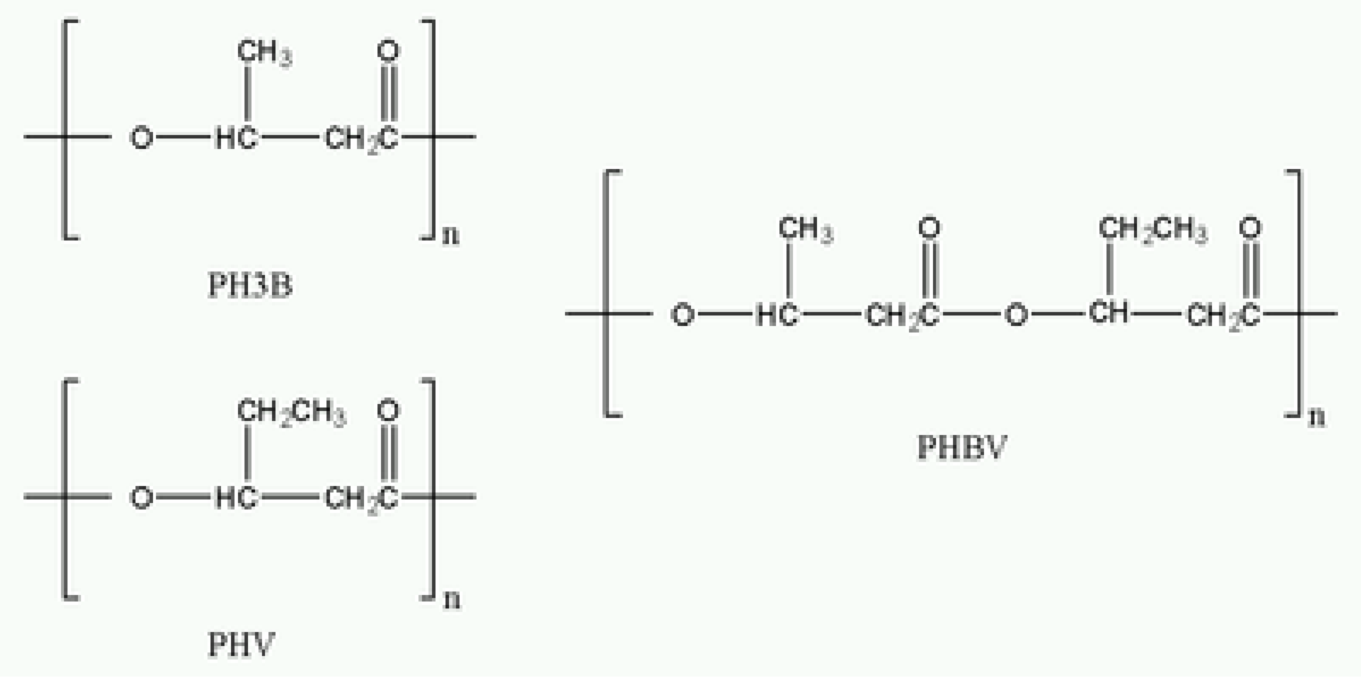
- whey (lactose, salt conditions)
- glycerol
- bone and meat meal (N source)
- animal fats



Polyhydroxyalkanoates (PHA)

- Monomer: β-hydroxy acids
  → Large variety of structures
    - Poly(β-hydroxy butyrate)
    - Poly(β-hydroxy butyrate-co-valerate)
    - Poly(β-hydroxy butyrate-co-hexanoate)

    Etc.



bio-on

PHAs produced by BIO-ON

Using MINERV PHAs (Polyhydroxyalkanoates developed using beets) Bio-on has identified the possibility of producing a new family of naturally biodegradable polyesters derived from sugar beets. The MINERV PHAs logo identifies the product that will in turn be marked and protected by their specific characterization and subsequently sold or licensed to third parties.
Polyhydroxyalkanoates or PHAs is a linear polyester produced in nature by bacterial fermentation of sugar. More than 100 different monomers can be joined by this family to create materials with extremely different properties. Thermoplastic or elastomeric materials ca be created with melting points ranging from 40 to 180° C. MINERV-PHA is a high-performance PHAs biopolymer. MINERV "spheres" in white represent the MINERV-PHAs biopolymer obtained from sugar beets. These elements are the result of bacteria nourished by beet juices. Recovery is the next step in the process (recovery of PHAs) when Polyhydroxyalkanoates are recovered and separated from the rest of the organic material of the cell. All waste materials (small amounts) are put back into the production cycle to feed new bacterial colonies along with the intermediate beet juice (exclusive Bio-on patent).

NATURAL BIODEGRADATION IN WATER

WATER OK biodegradable VINÇOTTE

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 98%

Bio-on concede in licenza la possibilità di produrre **MINERV-PHA™** per realizzare

Polyhydroxyalkanoato o **PHAs** sono un poliestere lineare prodotto in natura da una fermentazione batterica di zucchero.

Più di 100 differenti monomeri possono essere uniti da questa famiglia per dare vita a materiali con proprietà estremamente differenti.

Possono essere creati materiali termoplastici o elastomerici, con il punto di fusione che varia da 40 a oltre 180°C.

MINERV-PHA è un biopolimero PHA ad elevata prestazione. **MINERV-PHA** ha ottime proprietà termiche. Attraverso la caratterizzazione è possibile soddisfare esigenze produttive da -10°C a +180°C. Il prodotto è particolarmente indicato per la produzione di oggetti attraverso metodi di produzione ad iniezione o estrusione. Sostituisce inoltre prodotti altamente inquinanti come **PET, PP, PE, HDPE, LDPE**.

BIODEGRADABILITA' NATURALE IN ACQUA

SECTOR WEAKNESS

25 gennaio 2016 - Aggiornato alle 08.04

Zucchero, annuncio di Eridania Sadam: campagna sospesa a San Quirico

Basso prezzo di mercato dello zucchero e scarsa superficie effettivamente seminata alla base della scelta. LO stabilimento di Trecasali mantenuto per una eventuale ripresa dell'attività nel 2017. Incognite sul futuro dei 100 dipendenti e dei 200 lavoratori stagionali

PRICE VOLATILITY

Zucchero, Eridania Sadam riprende la campagna di raccolta a Trecasali

Il Gruppo Maccaferri continua nell'attività di studio per lo sviluppo dello stabilimento di San Quirico in una bio-raffineria

SOLUTION: BIOREFINERY

Home . Sostenibilita . World in Progress . Sostenibilità: intesa Bio-on-Eridania Sadam per produrre molecola chimica verde

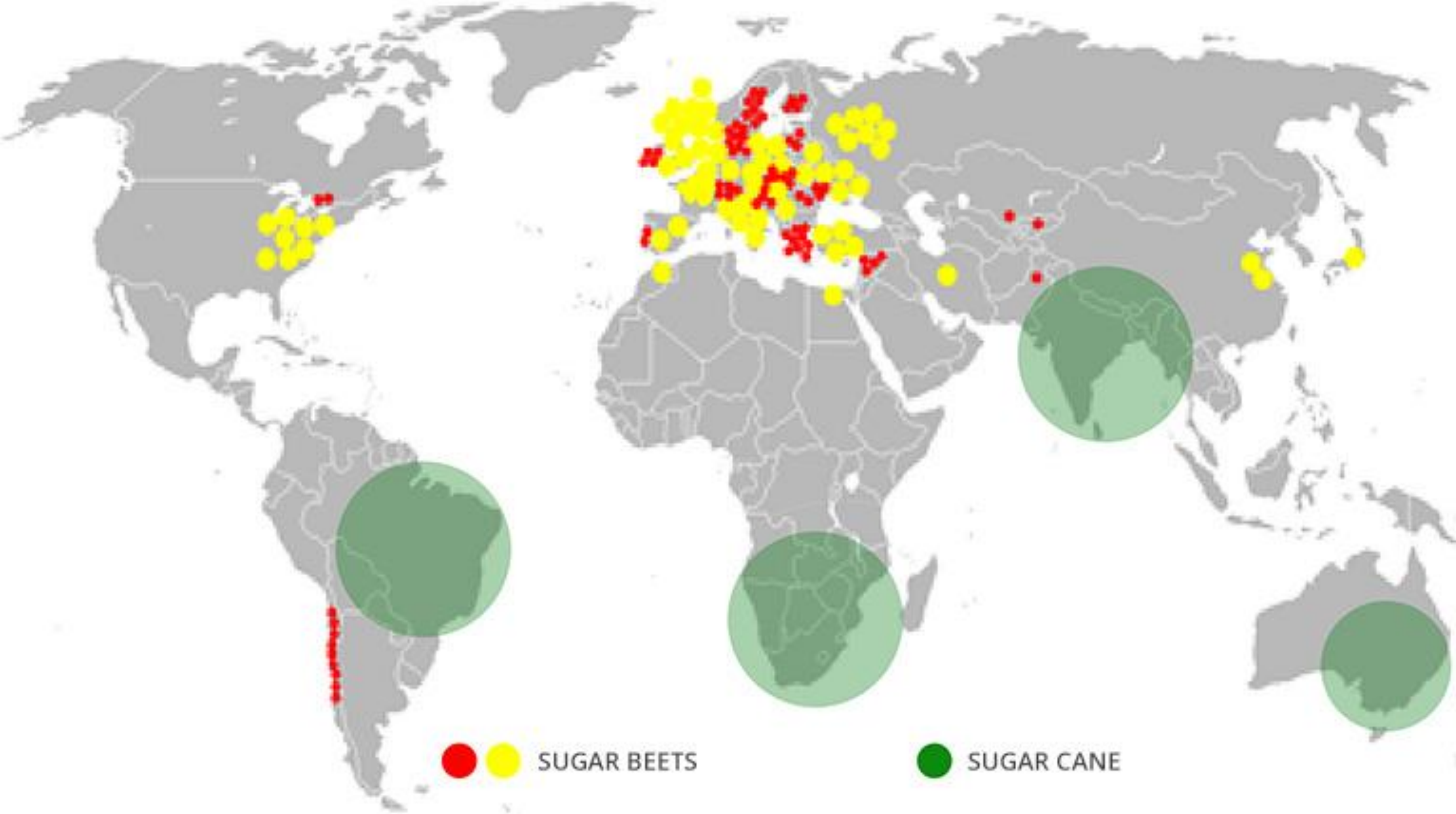
Sostenibilità: intesa Bio-on-Eridania Sadam per produrre molecola chimica verde

WORLD IN PROGRESS

Pubblicato il: 16/02/2015 18:47

Insieme per produrre acido levulinico, una molecola chiave per la futura chimica sostenibile e a basso impatto

WHERE



minerv.

MISSION

Bio-on nasce nel 2007 con l'intento di operare nel settore delle moderne Biotecnologie applicate ai materiali di uso comune con lo scopo di dare vita a prodotti e soluzioni completamente naturali, al 100% ottenuti da fonti rinnovabili o scarti della lavorazione agricola.

PHAs: Polidrossialcanoati (plastica veramente biologica) e relative applicazioni strategiche a 360° (packaging generico, packaging alimentare, design, abbigliamento, automotive).

TARGET: Il target di riferimento di Bio-on è operare direttamente nel mondo agro alimentare, nel settore del design e degli accessori, nel settore della cosmetica, nel settore farmaceutico fornendo a tutti la tecnologia necessaria per produrre o utlizzare PHAs con lo sviluppo delle relative caratterizzazioni.

PROGETTO: Intellectual Property Company con sede basata a Bologna e la possibilità di concedere licenze in tutto il mondo. Dalla sede di progettazione al pool di aziende di engineering e laboratori impegnati nella continua progettazione, produzione e distribuzione del know-how **Bio-on**. La produzione di PHAs è limitata territorialmente attraverso contratti di licenza d'uso della tecnologia o partnership industriali dedicate a specifiche aree commerciali. Per l'utilizzo della tecnologia Bio-on contattateci: **info@bio-on.it**

PRODUZIONE: Dal 2017 **Bio-on** opererà nella sua sede produttiva di Bologna dedicata alla creazione e produzione di prodotti PHAs speciali per applicazioni in ambito cosmetico e farmaceutico. Per l'acquisto dei prodotti speciali Bio-on contattateci: **info@bio-on.it**

WHAT ARE THE DRIVING FORCES BEHIND A BIO-LAMP?

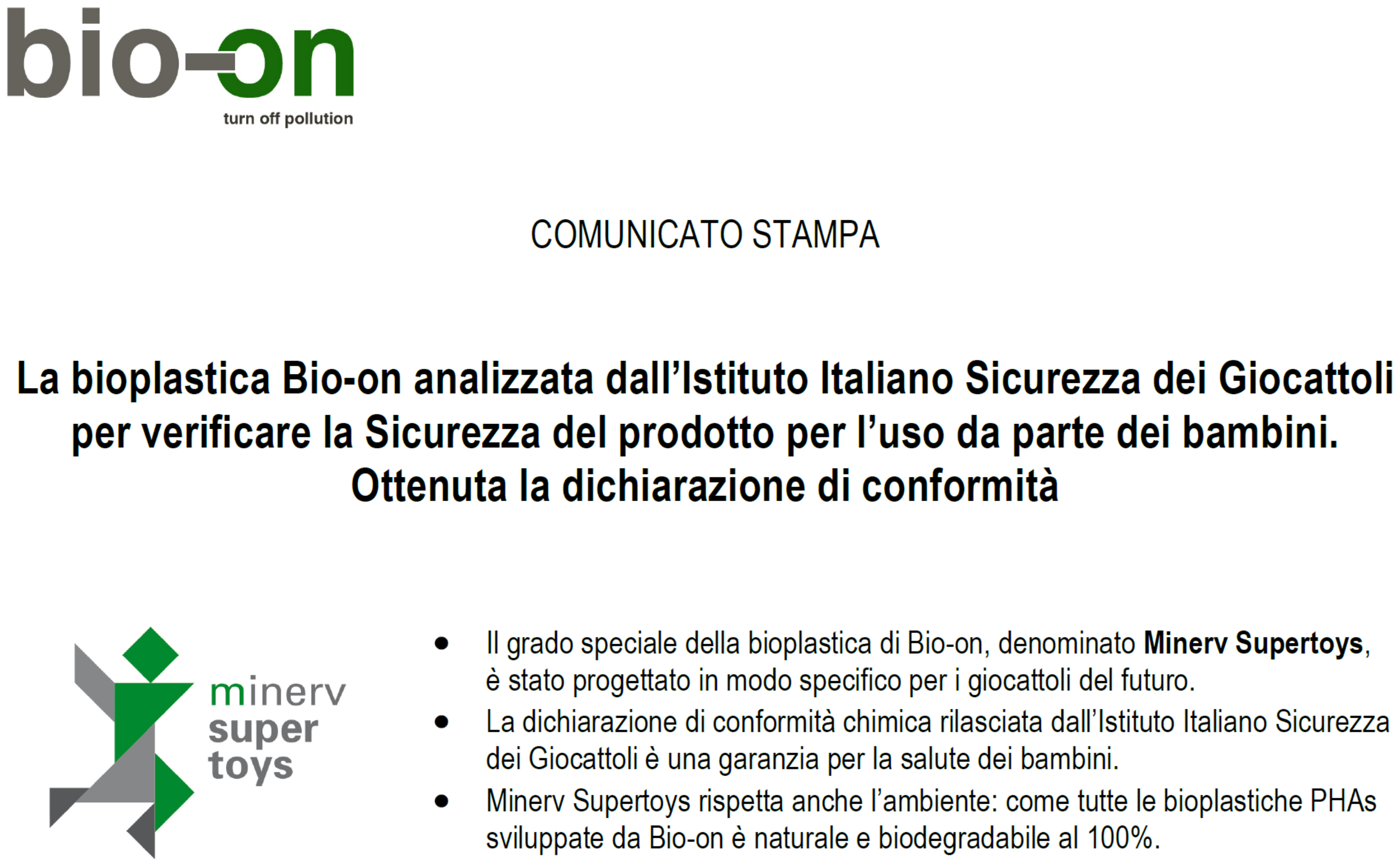
bio-on

FLOS

FLOS to be world's first company to use revolutionary bioplastic designed by bio-on

Miss Sissi, designed by Philippe Starck in 1991, is presented today in an innovative, completely biodegradable material, thanks to the global collaboration between the two companies

http://www.bio-on.it/mission.php

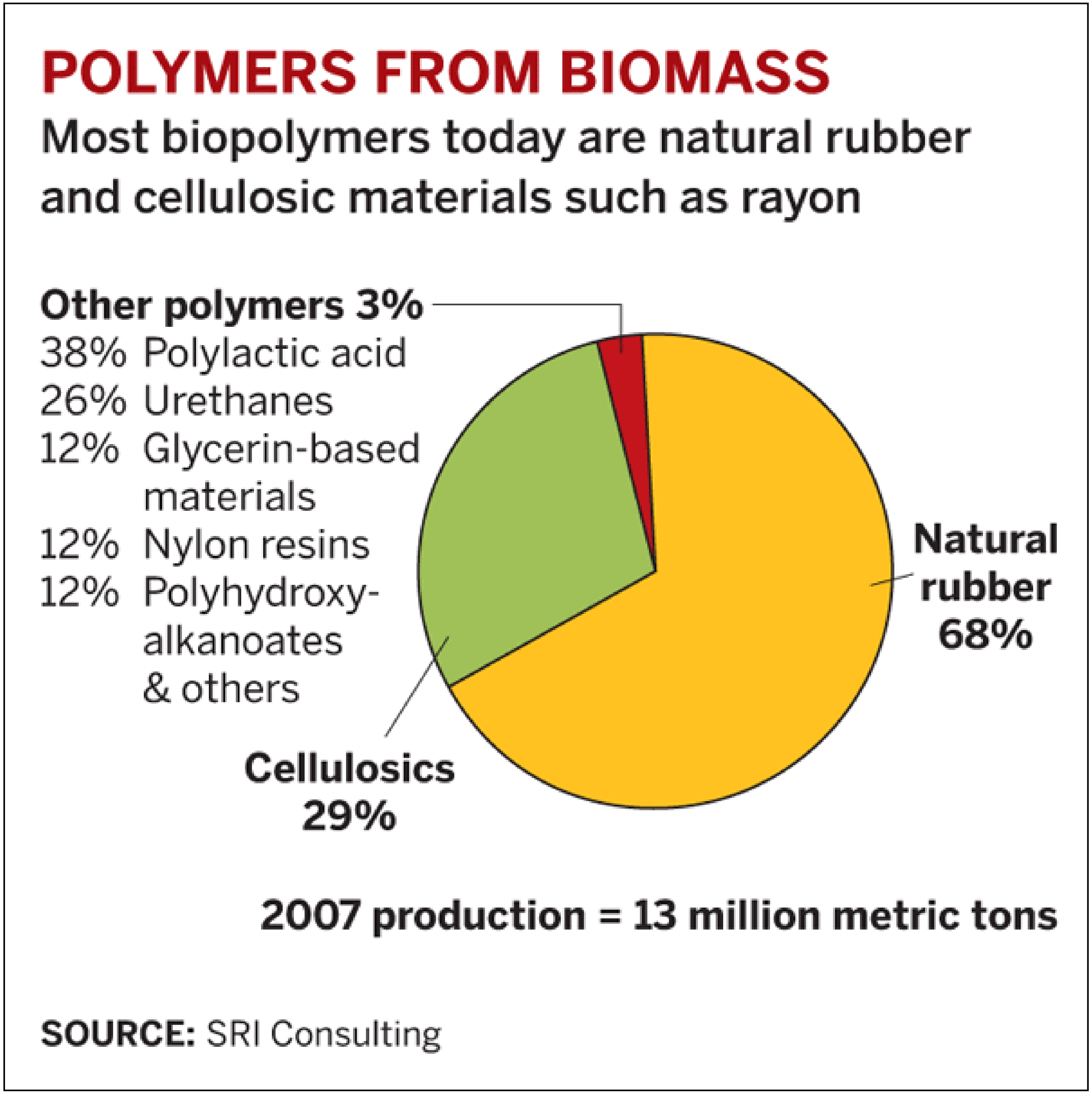


COMUNICATO STAMPA

La bioplastica Bio-on analizzata dall'Istituto Italiano Sicurezza dei Giocattoli per verificare la Sicurezza del prodotto per l'uso da parte dei bambini. Ottenuta la dichiarazione di conformità

- Il grado speciale della bioplastica di Bio-on, denominato **Minerv Supertoys**, è stato progettato in modo specifico per i giocattoli del futuro.
- La dichiarazione di conformità chimica rilasciata dall'Istituto Italiano Sicurezza dei Giocattoli è una garanzia per la salute dei bambini.
- Minerv Supertoys rispetta anche l'ambiente: come tutte le bioplastiche PHAs sviluppate da Bio-on è naturale e biodegradabile al 100%.

Situation



POLYMERS FROM BIOMASS

Most biopolymers today are natural rubber and cellulosic materials such as rayon

2007 production = 13 million metric tons

SOURCE: SRI Consulting

ORANGE FIBER

Adriana immagina per la sua tesi un tessuto sostenibile dagli agrumi. Condivide l'idea con Enrica e con tanta creatività e voglia di osare danno vita ad Orange Fiber

IL BREVETTO
Dallo studio di fattibilità condotto con il Politecnico di Milano si sviluppa il brevetto, che viene depositato in Italia ed esteso a PCT internazionale.

A dicembre 2015, grazie anche al finanziamento Smart&Start di Invitalia, viene inaugurato il primo impianto pilota per l'estrazione della cellulosa da agrumi.

ORANGE FIBER X FERRAGAMO

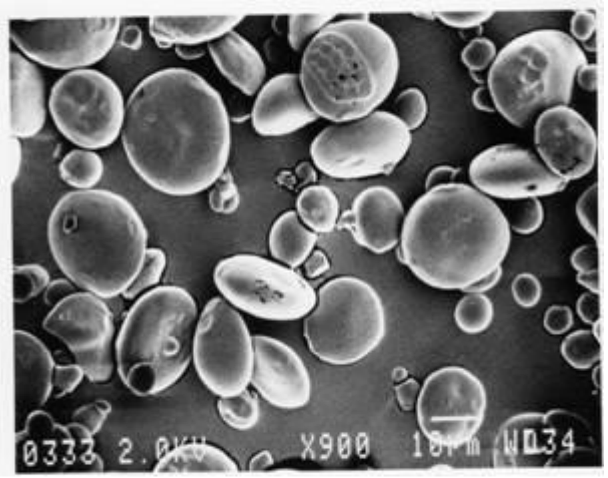
Ferragamo Orange Fiber Collection

Dall'amore per l'innovazione, il design e la creatività italiana, nasce una collaborazione unica: la *Ferragamo Orange Fiber Collection*. Coerente al proprio motto, *Responsible Passion*, Salvatore Ferragamo ha colto per primo l'essenza e le potenzialità espressive del tessuto da agrumi, dando vita ad una fresca Capsule Collection, omaggio alla creatività mediterranea.

La collezione

Thermoplastic starch

based plastics



L. Averous, University Strasbourg:
www.biodeg.net/biomaterial.html

Starch polymer structure retained while granular structure is destroyed under influence of heat, mixing and plasticizers (e.g. water, glycols)

Used in composites, blends, multilayers

Biodegradable

Organic waste collection, vapour permeable packaging

Mater-bi (Novamont) 60.000 t/a cap.
Foamed starch for packaging

COS'E' IL MATER-BI®

Polimero Biodegradabile e Compostabile
Mater-Bi®: la prima famiglia di biopolimeri che utilizza componenti vegetali come l'amido di mais, preservandone la struttura chimica

Attraverso un processo di "complessazione" dell'amido con quantità variabili di agenti complessanti biodegradabili (naturali, da fonte rinnovabile, da fonte sintetica o mista), vengono create diverse sovrastrutture molecolari caratterizzate da un'ampia gamma di proprietà.

Mater-Bi® è prodotto nello stabilimento di Terni, in forma di granulo e può essere lavorato secondo le più comuni tecnologie di trasformazione, per realizzare prodotti dalle caratteristiche analoghe o migliori rispetto alle plastiche tradizionali, ma perfettamente biodegradabili e compostabili, minimizzando l'impatto ambientale. I prodotti in Mater-Bi® dopo l'uso si biodegradano nel tempo di un ciclo di compostaggio.

LA STORIA (1989)

MONTEDISON

Montecatini
Tecnologie
Chimiche

Eridania-Beghin Say
Materie Prime
Agricole

FERTEC Ferruzzi
Research and
Technologies

PROGETTI DI RICERCA&SVILUPPO CON FOCUS SU:
MATERIALI, COBUILDERS PER DETERGENZA,
BIOCARBURANTI, ADDITIVI PER CARTA, INTERMEDI
CHIMICI DA HYDROCRACKING, ETC.

Novamont affonda le proprie radici nella scuola di Scienza dei Materiali Montedison e che nasce nel 1989 per l’integrazione tra chimica, ambiente e agricoltura attraverso l’impiego di fonti rinnovabili per la produzione di bioplastiche per applicazioni specifiche a basso impatto ambientale.

La storia

2005

Lancio di Pneo, innovativo sacchetto in MATER-BI

2007

Premio "European Inventor of the Year"

2012

Prodotti Foodservice in MATER-BI alle Olimpiadi di Londra

Acquisizione Centro Ricerca di Piana di Monte Verna

Raccolta umido con sacchi MATER-BI a Milano

2014

Lancio primi prototipi sacchi di nuova generazione ad Ecomondo

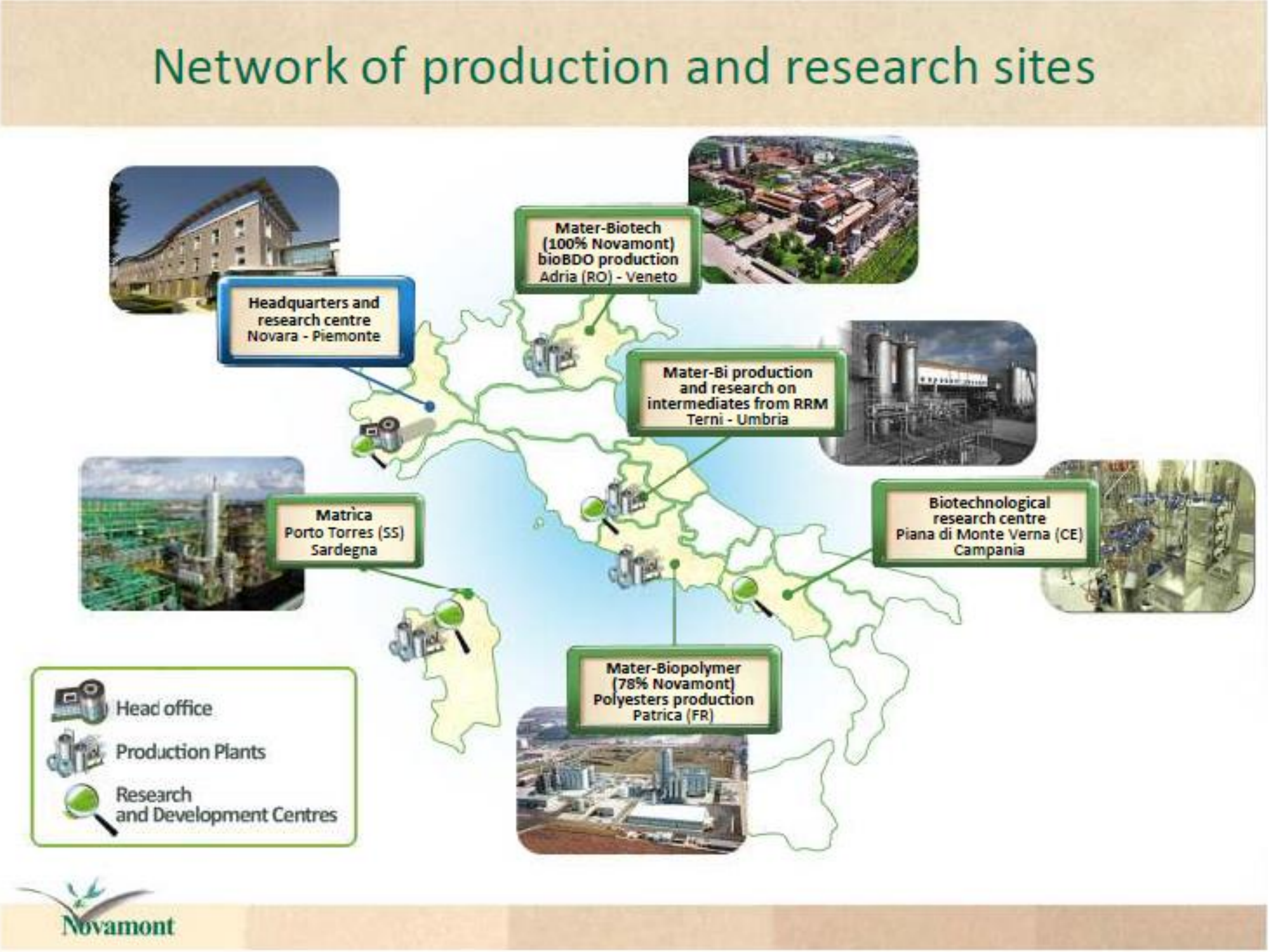
Sacchi Frutta e Verdura in MATER-BI in Unicoop Firenze

2015

Lavazza - Capsula Compostabile

Nuovo Brand

Prodotti Foodservice in MATER-BI per Eataly ad Expo Milano



Network of production and research sites

Headquarters and research centre
Novara - Piemonte

Mater-Biotech
(100% Novamont)
bioBDO production
Adria (RO) - Veneto

Mater-Bi production and research on intermediates from RRM
Terni - Umbria

Matrìca
Porto Torres (SS)
Sardegna

Biotechnological research centre
Piana di Monte Verna (CE)
Campania

Mater-Biopolymer
(78% Novamont)
Polyesters production
Patrica (FR)

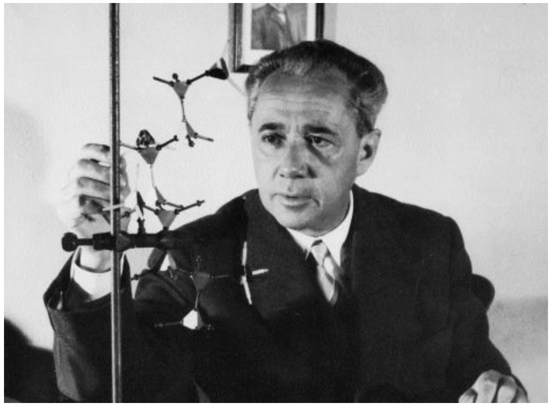
Head office

Production Plants

Research and Development Centres

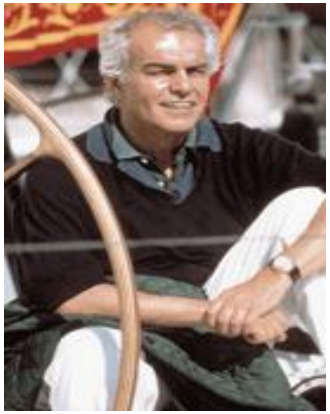
Luigi Capuzzi
luigi.capuzzi@novamont.com

Italian chemistry has a long lasting tradition of visionary innovators



Giulio Natta

Enrico Mattei



Roul Gardini

Guido Ghisolfi

Old bioplastics

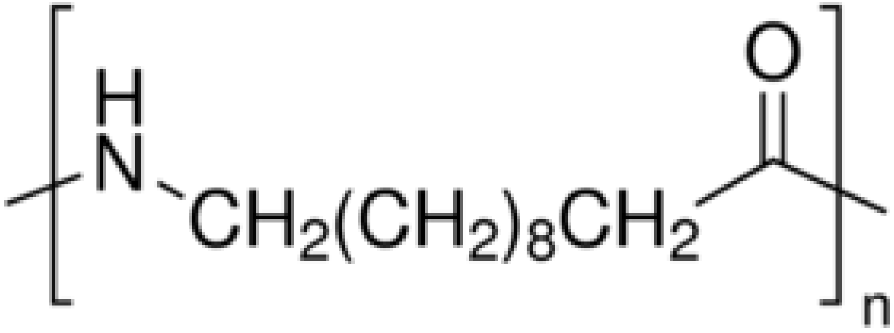
BIOPLASTICS ARE NOT NEW !!!

How polymer chemistry got started

- 1869 Nitrocellulose Hyatt Billiard balls

- 1897-1900 Casein - Galalith Casein + formaldehyde
- Nylon 11: 1930 11amino-undecanoic acid from castor oil

Nylon 11



- Polyamide
- Excellent resisitance to water
- Based on aminoundecanoic acid from castor oil (no better synthetic way!)

- Not biodegradable

- Oldest “active “ biobased plastic (1930s on)

(X 10.000 tonnes production)

Cellulose based

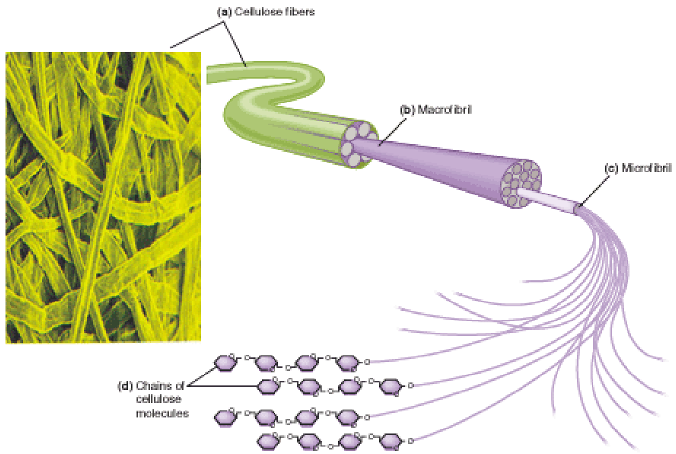
Polymeric nature of cellulose retained

Chemical modification disrupts native packing of cellulose molecules

Biodegradability normally lost upon modification

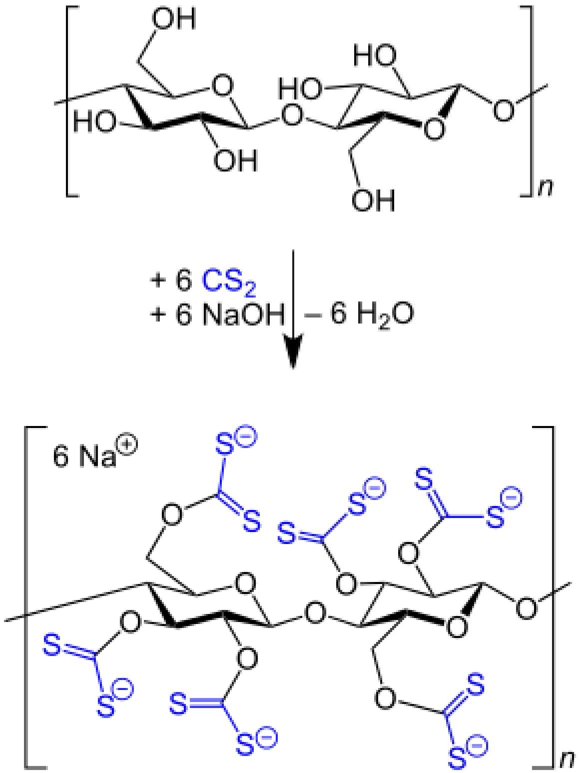
Viscose, cellulose acetate….

Innovia Natureflex



Source: Hercules Inc.: www.aqualon.com

Viscose:

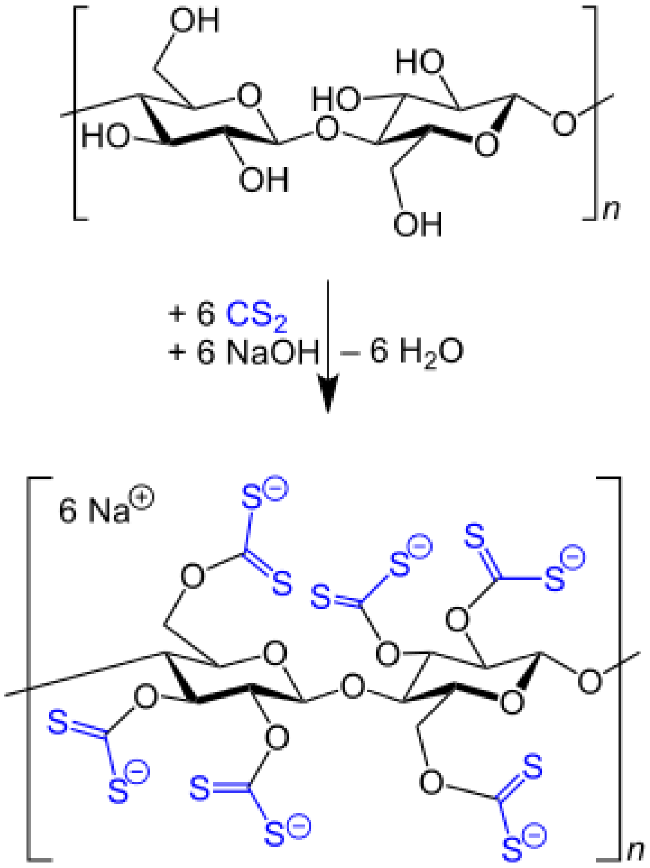


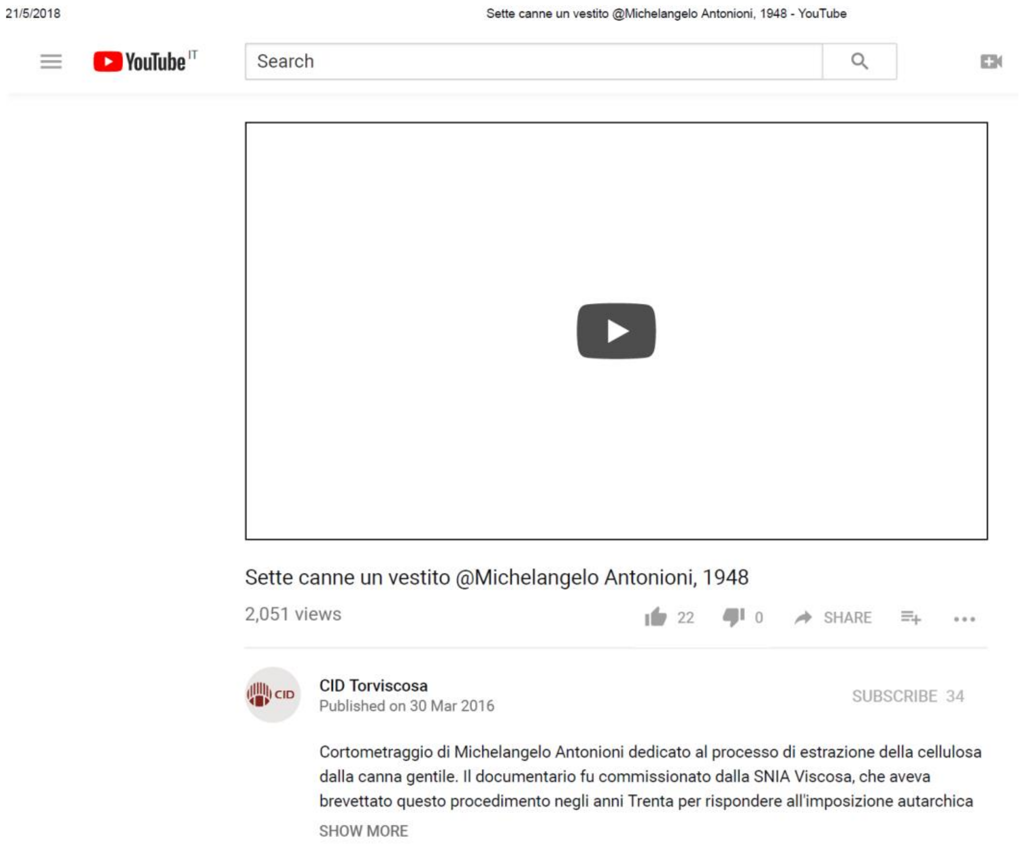
La viscosa viene prodotta dalla polpa di legno, dal cotone e dalla paglia, trattati con una soluzione di NaOH;
viene quindi aggiunto solufuro di carbonio (CS_2) e si forma xantogenato di cellulosa che viene ulteriormente disciolto con altra soda caustica.

La soluzione colloidale viene estrusa
I filamenti che escono dalla filiera formano il filo singolo che viene roccato sulla macchina di filatura.
In seguito la rocca viene caricata in cantra del lavaggio e poi questo filo lavato ed asciugato su appositi cilindri a vapore è pronto per le lavorazioni tessili del rayon.
Facendo passare questa soluzione in una sottile fessura posta in un bagno di acido solforico si può ottenere il cellophane.

Patented in 1894 in Englan, artificial silk.
Since 1924 named rayon.

La Viscosa e Torviscosa




21/5/2018 Sette canne un vestito @Michelangelo Antonioni, 1948 - YouTube

Sette canne un vestito @Michelangelo Antonioni, 1948

2,051 views

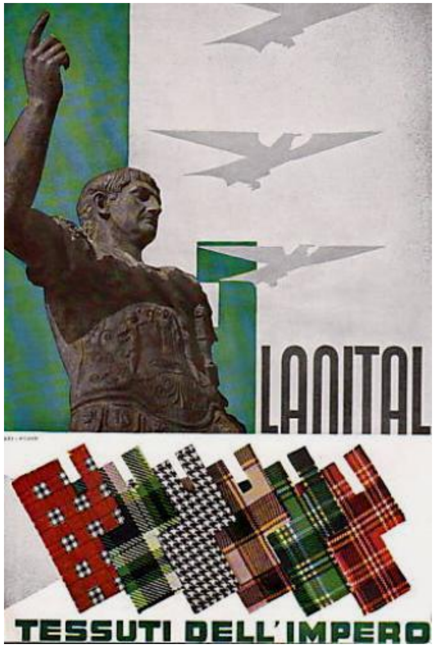
CID Torviscosa
Published on 30 Mar 2016

Cortometraggio di Michelangelo Antonioni dedicato al processo di estrazione della cellulosa dalla canna gentile. Il documentario fu commissionato dalla SNIA Viscosa, che aveva brevettato questo procedimento negli anni Trenta per rispondere all'imposizione autarchica

SHOW MORE

https://www.youtube.com/watch?v=vDcvrZ62IGM

LANITAL



ARACA (E. FORLIVESI)
Leumann Lanital - I Tessuti dell'Impero
1937 - n. inv. 11512

Lanital:
1935, fibra autarchica tratta dalla caseina
(Antonio Ferretti)

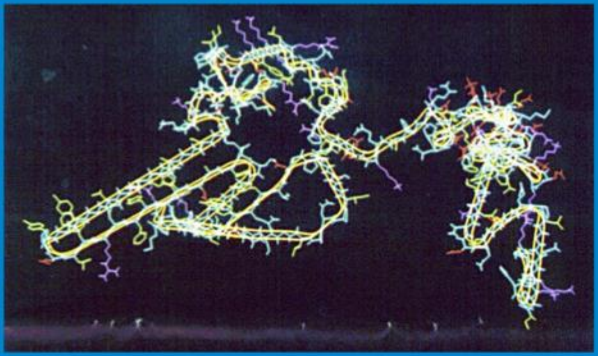
Nel frattempo negli USA la Atlantic Researcg Associates Inc. produsse una fibra simile

Fibra proteica con struttura molecolare simile alla lana

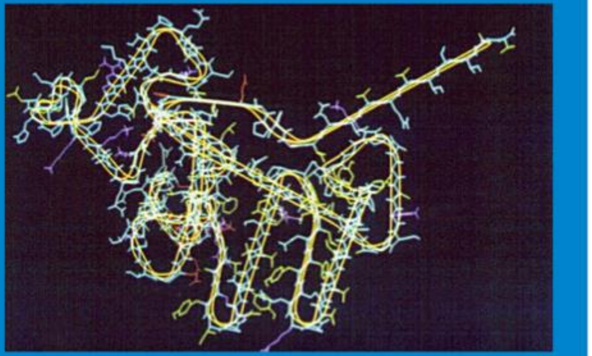
Nel dopoguerra la SNIA tentò di migliorare il prodotto e di rilanciarlo con il nome commerciale di *Merinova*, ma nel frattempo lo sviluppo delle fibre chimiche (acido acrilico) fece uscire dal mercato le fibre caseiniche.
Negli anni 2000, invece, questo materiale è stato riscoperto soprattutto per le sue qualità anallergiche, per la fabbricazione di prodotti per primissima infanzia o per chi ha forme di intolleranza per la lana e per le fibre sintetiche.

Le caseine non coagulano con il calore; per questo motivo non subiscono perdite significative durante la pastorizzazione o la sterilizzazione del latte. Le caseine coagulano invece per acidificazione o per l'azione di alcuni enzimi proteolitici.

α (s)-Caseina



K-Caseina



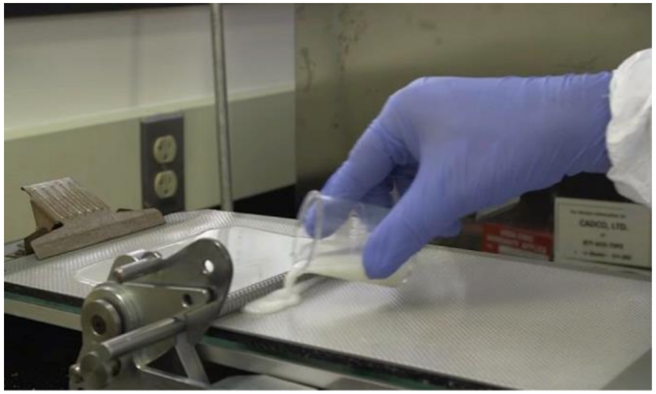
Qmilk

Make it from milk

November 12th, 2013 / By: Anke Domaske, Janet Preus / Featured

A lot of milk in the world is simply thrown away as unsuitable—for food, that is. German-based company Qmilch IP GmbH has found a use for discarded milk: fabric. In fact, it makes a silky smooth, beautiful fabric desirable for high fashion, appealing to high-end consumers who are not only interested in the ecology, but in the economic and social responsibility supporting the fashionable collections.

In addition to apparel, the fibers are particularly suitable for use in home textiles, the automobile industry and medical technology, and they offer advantages as well for thermal insulated seat covers or hygienic diaphragms. With interest in, and the use of, these textile fibers growing, supply is challenged to meet the demand.



La fase di produzione di questi ecoimballaggi di nuova generazione, messi a punto presso il Dipartimento dell’Agricoltura degli Usa, ha di recente preso il via con una prima linea da parte di una piccola azienda texana, ma già altre realtà stanno guardando con interesse ai nuovi imballaggi.

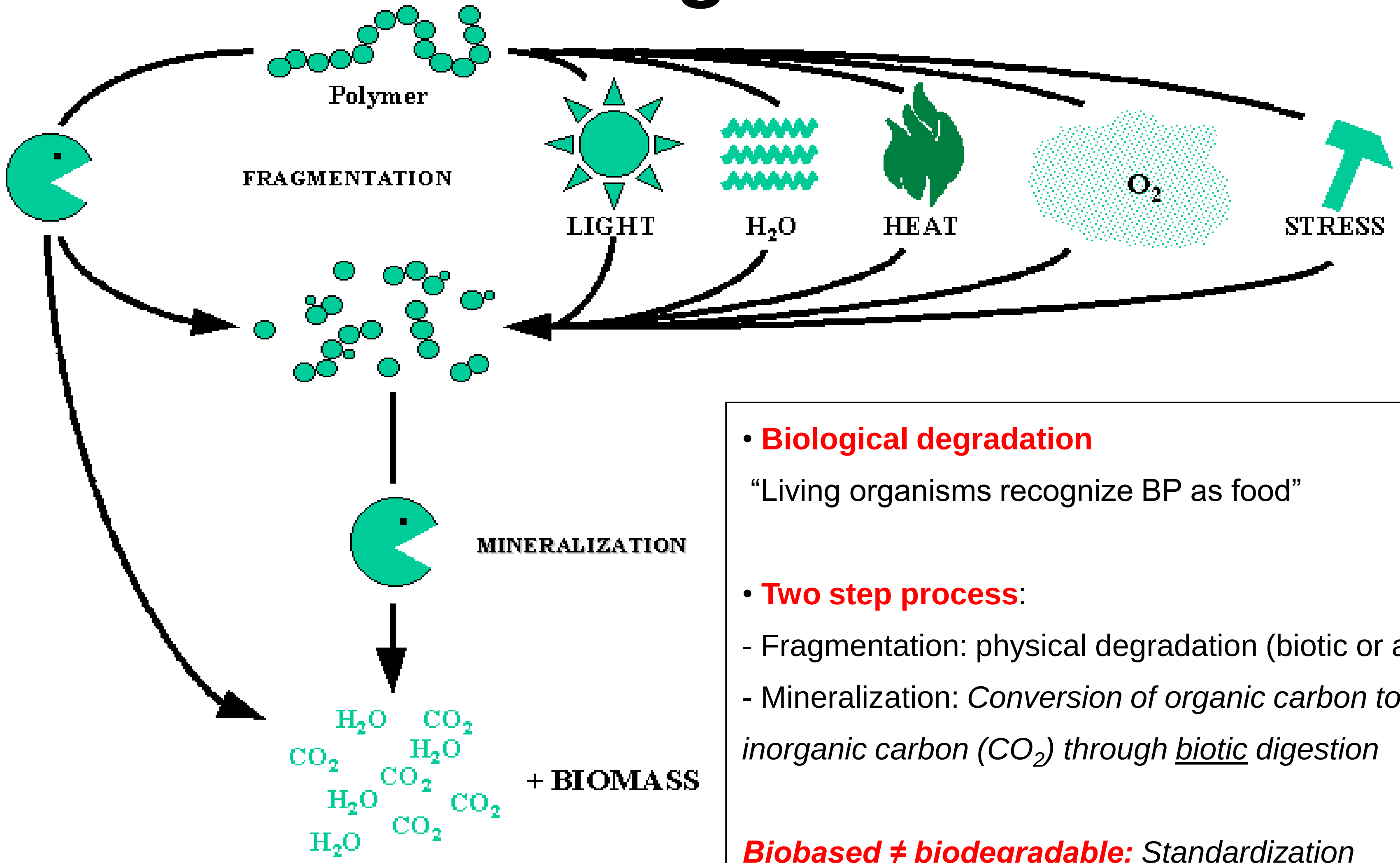
Per il momento non si conosce ancora molto del processo di produzione perché i ricercatori hanno deciso di concentrarsi soprattutto sulla comunicazione dei vantaggi nell’utilizzo dei nuovi imballaggi a base di caseina. In particolare sul fatto che potranno ridurre i problemi provocati dalla diffusione ormai incontrollata di rifiuti di plastica nell’ambiente.

Secondo la coordinatrice del progetto, questo tipo di pellicola basata su proteine riduce di 500 volte la diffusione di ossigeno rispetto ai film in uso e garantirebbe “una migliore conservazione dei cibi nella catena della distribuzione e riducendo di conseguenza gli sprechi”.

Annex 1

Biodegradability and compostability

Biodegradation



- **Biological degradation**

  "Living organisms recognize BP as food"

- **Two step process**:

- Fragmentation: physical degradation (biotic or abiotic)
- Mineralization: *Conversion of organic carbon to inorganic carbon (CO_2) through biotic digestion*

Biobased ≠ biodegradable: *Standardization*

Testing

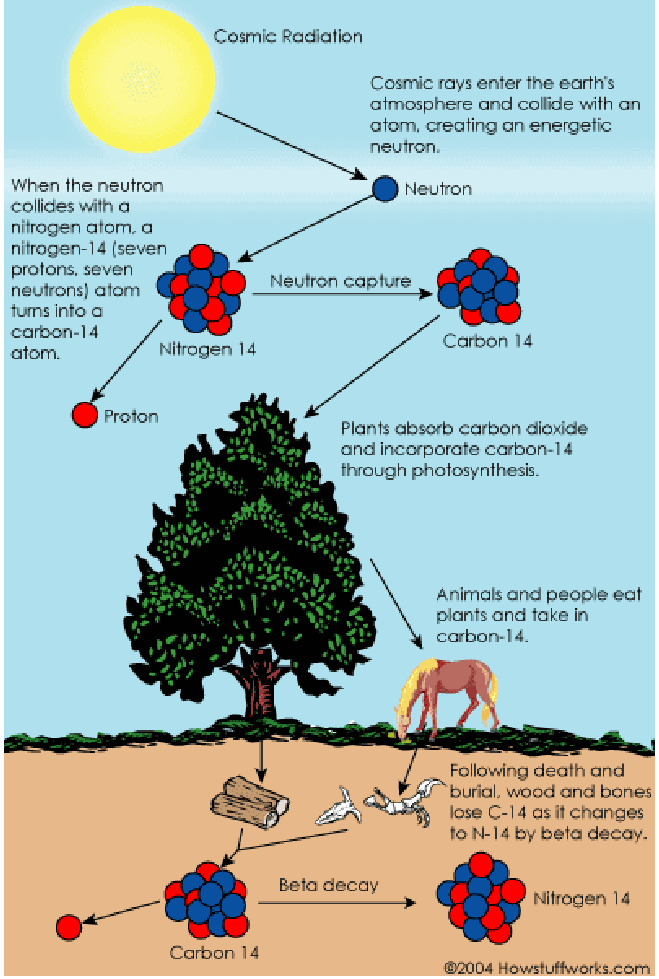
Determination of biobased carbon content

- Measurement of C^{12} / C^{14} ratio

  C14 is formed in atmosphere and is characteristic of biobased carbon while it dimminished in fossil sources
- C^{14} $t_{1/2}$ = 5730 years
- After 50.000 years very low conc.

ASTM D6866 - 08

Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis



La biodegradazione in ambiente naturale

La biodegradazione, il processo naturale che permette il riciclo delle sostanze organiche, può avvenire in ambienti differenti: il suolo, i corsi d’acqua, il mare.

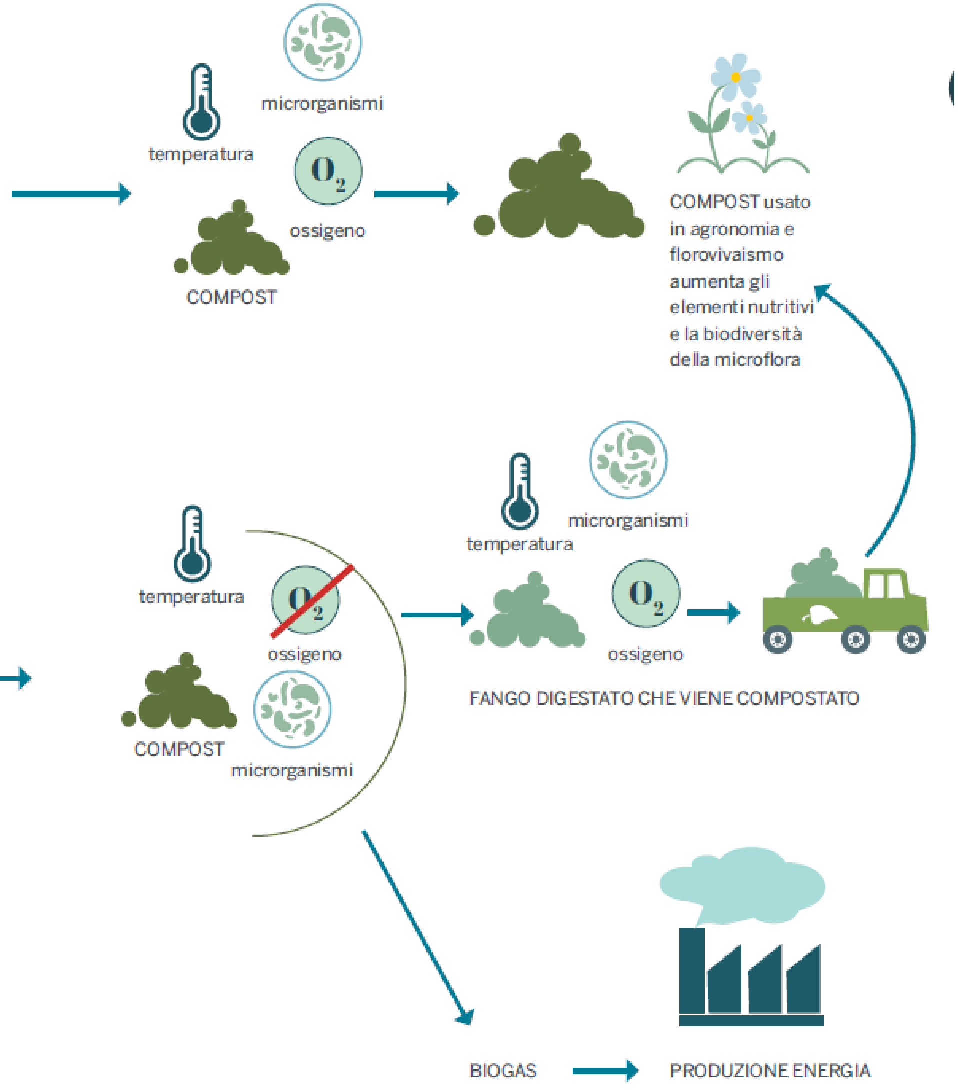
compostabilità

IL COMPOSTAGGIO

Questo processo ha luogo in ambiente a umidità e temperatura controllate, in presenza di ossigeno. Le maggiori quantità di rifiuti organici sono trattate in impianti industriali in cui i processi di compostaggio raggiungono temperature di 70°C. Quando il compostaggio è operato individualmente, come attività di giardinaggio su piccola scala, viene chiamato "compostaggio domestico" nel quale si raggiungono temperature meno elevate.

LA DIGESTIONE ANAEROBICA

È un altro processo di trattamento dei rifiuti organici. La sostanza organica è degradata da parte di microrganismi, in assenza di ossigeno, e si trasforma in biogas, utilizzabile per produrre energia e un fango chiamato digestato che, sottoposto a compostaggio dà origine a compost.



La compostabilità

È la capacità di un materiale organico, animale o vegetale, di decomporsi trasformandosi in una miscela di sostanze detta compost, utilizzata in agronomia come fertilizzante e ristrutturante del terreno. Il processo che porta alla formazione di questo ammendante agricolo è detto compostaggio.

COMPOSTAGGIO

Questo processo ha luogo in ambiente a umidità e temperatura controllate, in presenza di ossigeno.

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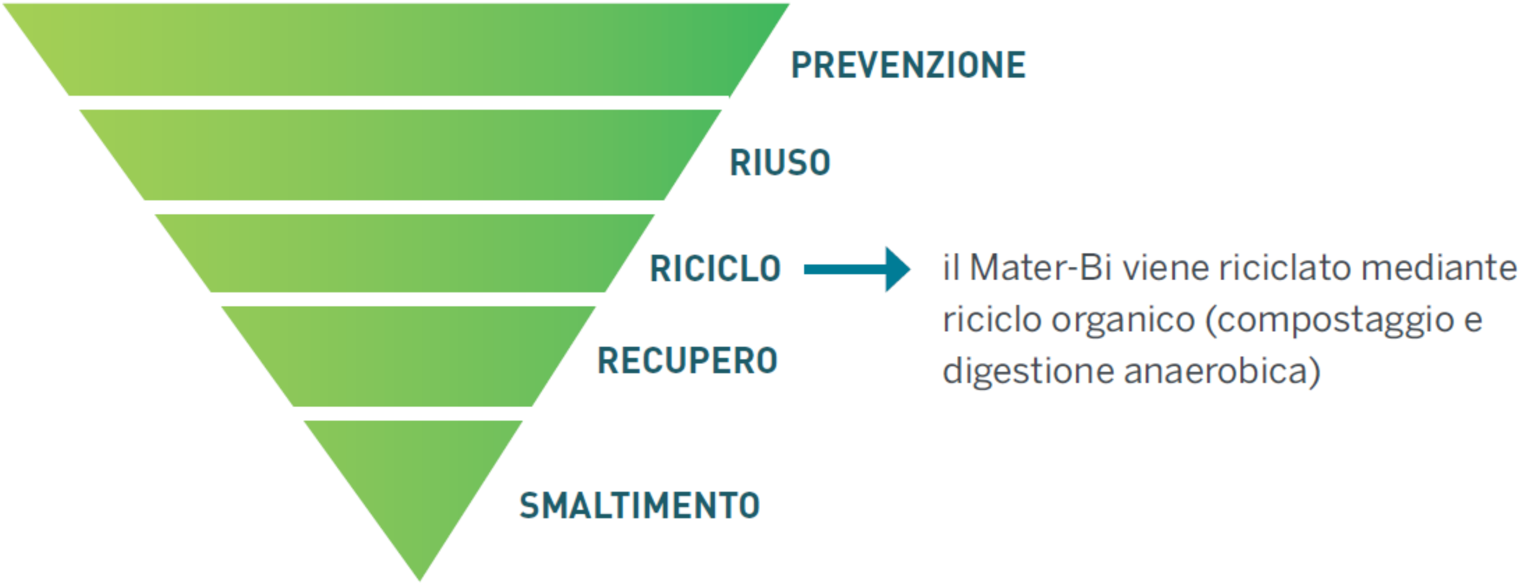
Digestione anaerobica

È un processo di trattamento dei rifiuti organici. La sostanza organica è degradata da parte di microrganismi, in assenza di ossigeno, e si trasforma in biogas, utilizzabile per produrre energia e un fango chiamato digestato che, sottoposto a compostaggio dà origine a compost.

GERARCHIA DEI RIFIUTI

Direttiva 98/2008 – Normativa comunitaria sulla gestione dei rifiuti



PREVENZIONE

RIUSO

RICICLO → il Mater-Bi viene riciclato mediante riciclo organico (compostaggio e digestione anaerobica)

RECUPERO

SMALTIMENTO

Nel campo dei metodi o dei processi è nata la verifica ETV (Environmental Technology Verification http://iet.jrc.ec.europa.eu/ etv/). Si tratta di un programma pilota che, tramite certificazione di terza parte indipendente, aiuta le aziende che hanno sviluppato tecnologie ambientali innovative a raggiungere il mercato.

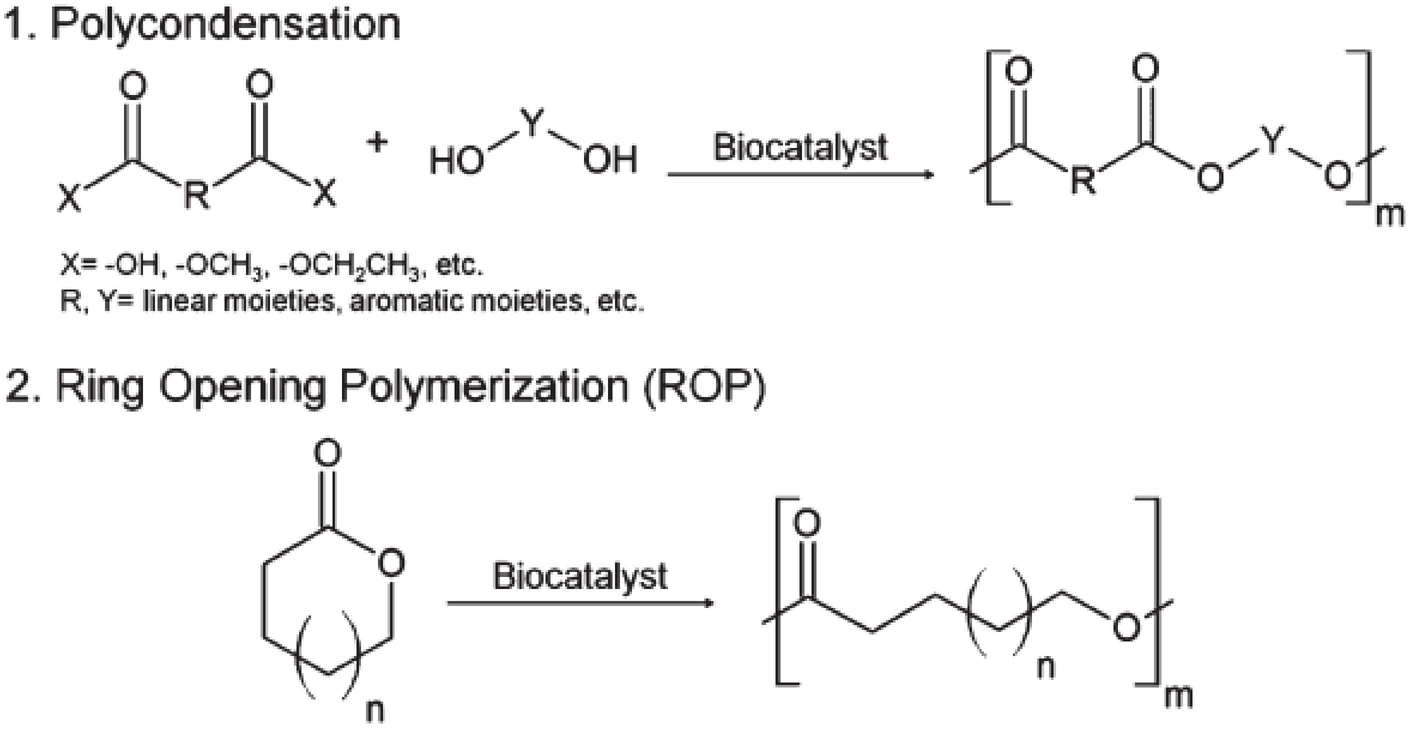
STANDARD

È il modello, la norma o l'insieme di linee-guida a cui si uniforma un prodotto o un'attività, in particolar modo per ciò che riguarda le performance tecniche e gli aspetti di qualità.

- **EN 16785-1:2015- Prodotti a base biologica – Contenuto di rinnovabili – parte 1: Determinazione del contenuto di rinnovabili mediante il metodo del Carbonio-14 e della composizione elementare.**
Lo standard dettaglia un metodo per la determinazione di sostanze rinnovabili attraverso l'analisi del Carbonio-14 e della composizione elementare del prodotto oggetto di studio.
- **EN 16760:2015 – Prodotti a base biologica – Life Cycle Assessment.**
Lo standard fornisce le specifiche indicazioni e i requisiti necessari per effettuare uno studio LCA su prodotti derivati da fonti rinnovabili, basato sulle norme ISO 14040 e ISO 14044.

Annex 2

Enzymatic synthesis of polesters



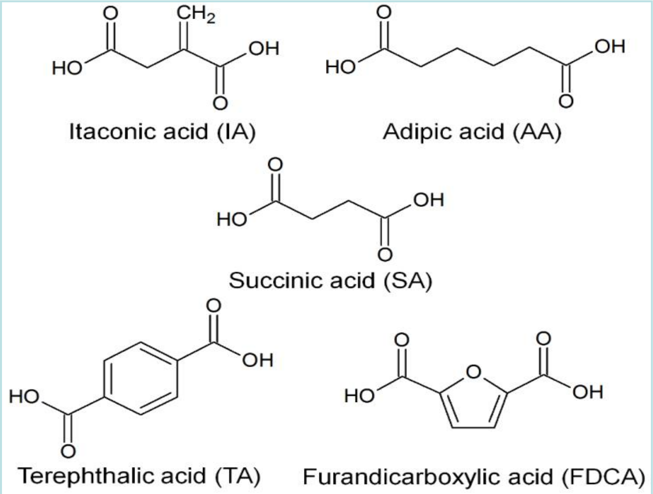
X= -OH, -OCH$_3$, -OCH$_2$CH$_3$, etc.
R, Y= linear moieties, aromatic moieties, etc.

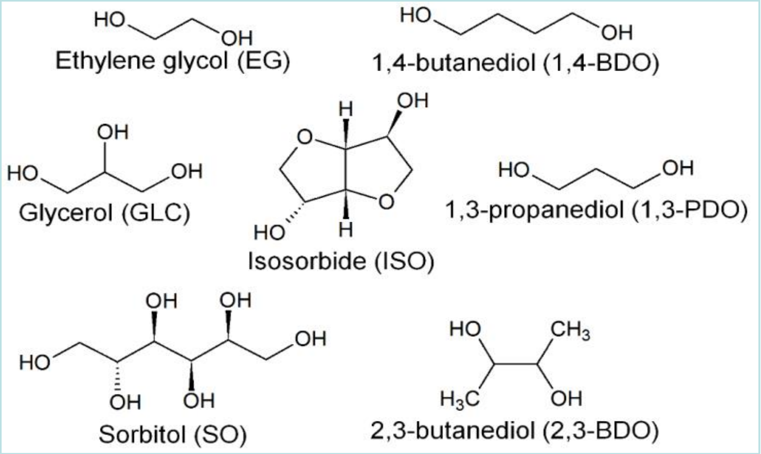
Scheme 3. Routes for the enzymatic synthesis of bio-based polyesters. (1) Polycondensation reaction of diacids (or their diesters) with polyols. (2) Ring-opening polymerization of lactones.

Why enzymes in polyester synthesis?

- **Selective and efficient under mild conditions**
- **No need of toxic metal catalysts**
- **Solvent-free processes feasible**

(Polycondensation)





Mn < 20000

- **Tailored pre-polymers for advanced functionalities**

R. A. Gross, et al., *Trends Biotechnol.*, 2010, **28**, 435-443
A. Pellis et al., *Trends Biotechnol.*, 2016, 34, 316-328.

Enzymes for polyester synthesis and functionalyzation