

Proprietary process technology

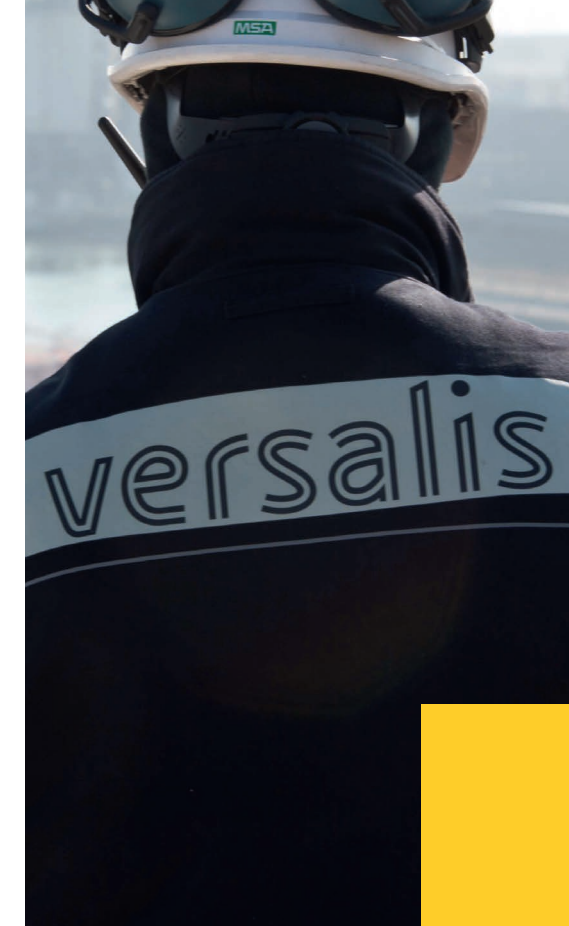
LDPE

Low Density Polyethylene

HIGH PRESSURE TUBULAR / AUTOCLAVE TECHNOLOGY



Versalis proprietary process technologies available for licensing



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Our company

Versalis – the petrochemical subsidiary of Eni – is a dynamic player in its industry sector facing the multifold market needs through different skills.

With a history as European manufacturer with more than 50 years of operating experience, Versalis stands as a complete, reliable and now global supplier in the basic chemicals, intermediates, plastics and elastomers market with a widespread sales network.

Relying on continuous development in its production plants as well as in its products, strengthening the management of the knowledge gained through its long industrial experience, Versalis has become a worldwide licensor of its proprietary technologies and proprietary catalysts. The strong integration between R&D, Technology and Engineering departments, as well as a deep market expertise, are the key strengths for finding answers to customers requirements.

Our commitment to excellence, in quality of our products and services, makes our company an active partner for the growth of customers involved in petrochemical business.

Through engineering services, technical assistance, marketing support and continuous innovation, our knowledge is the key strength to customize any new project throughout all phases.

Customers can rely on this strong service-oriented outlook and benefit from a product portfolio that strikes a perfect balance of processability and mechanical properties, performance and eco-friendliness.

Introduction to Versalis LDPE High Pressure technologies

High pressure ethylene polymerization is known since first polyethylene discovery (1933 - England). Since then, many advances have been introduced into technology.

Low Density PolyEthylene has been produced by Versalis with High Pressure technologies since 60s in several plants located in Italy and in France (some of them formerly CdF). Over the years Versalis has developed both proprietary Autoclave and Tubular High Pressure technologies.

Versalis LDPE High Pressure Tubular and Autoclave technology resins are available with different grades having a good balance between processability and mechanical properties, ranging from agricultural film cover, heavy duty and shrink films, injection grades and surface coating materials.

Even though LDPE High Pressure production technology can be considered to be well consolidated and mature, especially in the last decades, the market requirements in terms of quality and environmental impact of LDPE pushed Versalis R&D to continuously update its technology and product portfolio, by improving its key proprietary equipment and by optimising the process cycle. Presently installed LDPE plant capacity based on Versalis High Pressure Technology is about 1.6 million of ton per year.

An important role in plant design is played by environmental and safety issues. Versalis has developed and successfully installed in currently operating plants a proprietary designed safety system: the Pyrotechnical Safety System, which protects both autoclave reactor and high pressure separator from ethylene decomposition. The system is able to react in very few millisecond and to reduce drastically the likelihood for aerial explosion after decomposition events.

The key features of Versalis LDPE High Pressure Tubular / Autoclave technology are:

- flexibility and ability to face different conditions and constraints. An individually evaluation to offer the best solution, tailored to specific customers' needs;
- high flexibility in term of product mix, covering all the market applications and good quality constancy and reproducibility;
- plant design allows to change grade in the most versatile and safe way, limiting off spec grade production;
- minimum amounts and number of chemicals introduced in the process;
- chemicals not proprietary and easily available on the market;
- very low residual monomer and oligomer content in the final product;
- very high thermal efficiency, with great energy recovery;
- cleanness process with the adoption of pure additive feeding system into molten polymer without use of solvent. The result is an improved process with effect on both product quality and ease of operation;
- great attention to the environmental issues in design, according to the environmental identified BAT, and application of advanced solution in order to minimize environmental impact.

Versalis can always provide appropriate solutions to different client's needs thanks to its capabilities and experience in the following fields:

Research & development

The presence of a strong R&D team, located first in Milan since the early 70s and now in Mantova, the operation of several plants with different technology, the long lasting experience on LDPE marketing qualifies Versalis as an outstanding owner of process know-how. Reliable and updated facilities (analytical labs and equipment for polymer processing), allow



Versalis to continuously up-to-date the technology in order to support the LDPE business in a very competitive and demanding market scenario. Additional services are then available for potential Licensees, such as technical assistance, training, development of analytical methods, site assistance for start-up and follow up, development of tailor made products on demand.

Process design & operational experience

Process design is flexible and able to face different conditions and constraints. Any project is individually evaluated to offer the best solution, tailored to specific customers' needs.

Thermal and fluid-dynamic analysis (CFD) can be applied to the design of key equipment, such as reactors and ancillary equipment, high pressure zone and proprietary safety system. Technical solutions have been selected by Versalis on the basis of proven reliability and effectiveness for smooth operation.

In Versalis technology technical solutions are continuously updated following a constant program of process updating and improvement.

New solutions undergo severe industrial tests before being incorporated in the technology.

This procedure guarantee that our licensees (and Versalis itself) have a technology that keeps the highest standards of performances and reliability.

Mechanical design

Versalis Engineering Dept. has been working in close coordination with the Process Dept. since a long time. This fact has allowed development of unique and well sound engineering solutions for critical equipment that guarantee the best results in terms of mechanical reliability and process performances.

Wastes and emissions

For many years Versalis has been taking notice of Environmental Impact of its industrial plants. The design of the plant is carried out bearing in mind the need of minimizing the effluents, as this means more efficiency and lower environmental impact. The identified BAT for this specific process are adopted: degassing extruder and nitrogen flushing to reciprocating machines packing are fully applied. Gas emission during plant shutdown are avoided by means of proven plant shutdown logic which allows to store the excess of gas in the recycle section. The process produces oily waste water which can be treated in a standard bio-treatment. The organic solvent and spent oils are collected and they can be treated by an incinerator.

Waste air emissions from extrusion and storage section can be treated with a regenerative thermal or catalytic oxidizer, or directly sent, as combustion air, to other units like steam cracking boilers. Solid waste material, mainly constituted of polymer waxes, could be sold as by-product or destroyed by incineration.



Main process parameters

Tubular technology	per MT LDPE
Net raw material (ethylene + modifier - purge ethylene)	1,005 - 1,007 kg
Electricity	0.85 MWh
High Pressure Steam consumption	250 kg
Low Pressure Steam production	1,000 kg
Cooling water ($\Delta T + 5\text{ }^{\circ}\text{C}$)	200 m ³

The flexibility of Versalis LDPE High Pressure Tubular technology allows to provide with a single line convenient solution for a broad range of capacities.

Autoclave technology	per MT LDPE
Net raw material (ethylene + modifier - purge ethylene)	1,005 - 1,007 kg
Electricity	0.85 MWh
High Pressure Steam consumption	200 kg
Low Pressure Steam production	200 kg
Cooling water ($\Delta T + 5\text{ }^{\circ}\text{C}$)	200 m ³

The flexibility of Versalis LDPE High Pressure Autoclave technology allows to provide with a single line convenient solution for a broad range of capacities.

Industrial applications

Industrial References for Versalis Tubular Technology, owned and/or licensed are:

Location	Capacity (kt/y)	1 st start up date
Ragusa Plant (Italy)	40 - LDPE	1965
Ragusa Plant (Italy)	110 - LDPE	1970
Skikda Plant (Algeria)	50 - LDPE	1974
Navodari Plant (Romania)	60 - LDPE	1979
Gela Plant (Italy)	130 - LDPE	1981
Umm Said Plant (Qatar)	180 - LDPE	1996
Dunkerque Plant (France)	240 - LDPE/EVA	2011 (Autoclave converted to tubular)

Industrial References for Versalis Autoclave Technology, owned and/or licensed are:

Location	Capacity (kt/y)	1 st start up date
Gela Plant (Italy)	70 - LDPE	1963
Ferrara Plant (Italy)	110 - LDPE	1976
Maracaibo Plant (Venezuela)	70 - LDPE	1976
Bratislava Plant (Slovakia)	90 - LDPE	1977
Dunkerque Plant (France)	190 - LDPE	1978
Umm Said Plant (Qatar)	180 - LDPE	1980
Sines Plant (Portugal)	80 - LDPE	1981
Yeosu Plant (South Korea)	120 - LDPE	1990
Nagothane Plant (India)	80 - LDPE	1991
Mailiao Plant (Taiwan)	60 - LDPE/EVA	2000

The Riblene® LDPE product portfolio

The Versalis High Pressure technologies enable the production of LDPE with variable features in the range of product grades, such as:

- high processability;
- good mechanical properties;
- high rigidity.

Riblene® LDPE products portfolio cover the most challenging fields of application.

Blown and cast film

- industrial bags and heavy duty shrink films;
- agricultural films;
- general purpose films;
- packaging;
- lamination film.

Coating

- coating on paper and other substrates.

Injection moulding

- large complex moulding;
- low thickness articles;
- caps and closures;
- toys.

Process description

Versalis Tubular and Autoclave processes are based on high pressure free radical initiated polymerization of ethylene to give LDPE.

To ensure good product properties and to optimize conversion and production rates, the polymerization reaction is carried out at 2000-2600 bar (Tubular) / 1000-2000 bar (Autoclave) operating pressure and at 180-300 °C operating temperature.

Under these conditions, free radical sources as peroxides, injected into the reaction zone, can promote the polymerization of ethylene in such a way to give the initiation, and following on, the propagation of the polymer chain.

A certain amount of a further olefin, such as propylene or butene, or alkane as butane, are added to the reaction mixture to regulate the molecular weight of LDPE by means of their actions as growing chain terminators.

The polymerization reaction takes place in a tubular reactor (Tubular technology) or in a multi-zone mixed adiabatic vessel reactor (Autoclave technology).

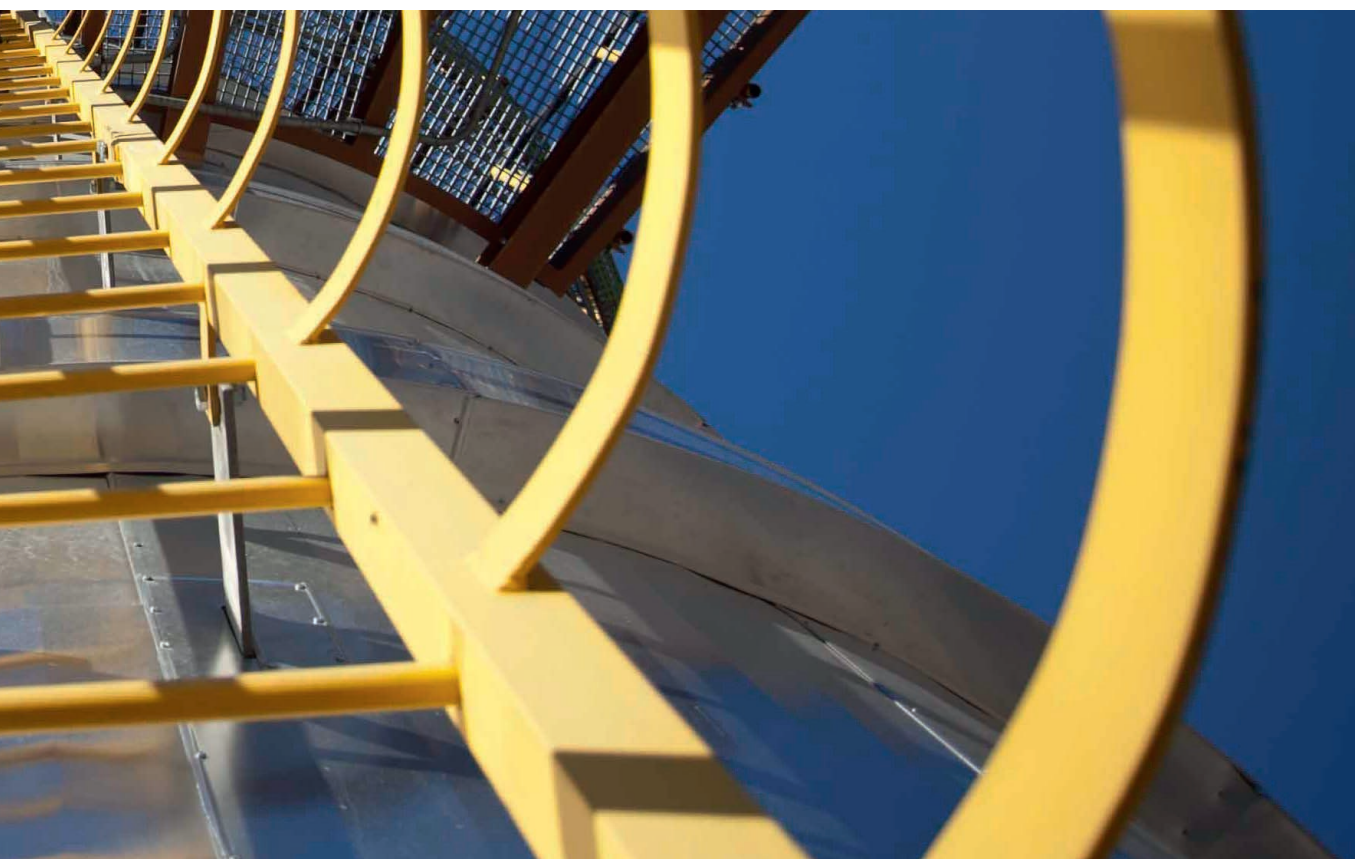
In Tubular technology, in order to ensure good polymer properties, the control of temperature in the reactor is achieved by a proper distribution, along the tubular reactor, of the reactants and catalysts injection points.

In Autoclave technology, the mixing of the reactants, which is the most critical parameter to ensure good polymer properties and to prevent undesired temperature or pressure rising, is provided by proprietary designed stirring device. The stirring device is composed by a motor stirrer suitable design and internal baffles to delimit the reaction zones that perform as adiabatic series of CSTRs.

After being discharged from the reactor (Tubular or Autoclave), the reaction mixture is fed to a separation section where polymer is separate from un-reacted gas and sent to the extruder.

The un-reacted gas mixture, after cooling and waxes and oil removal, is re-injected to the reactor inlet streams through different compression stages. Product is pelletized, dried, and sent to analysis bins; afterwards resin is blended and transferred by pneumatic convey to bagging silos or a bulk loading storage.

Plant configuration has been studied to reach the best balance between costs and benefits, to reduce the loss of material and effluent emission.



Process design advanced features

Versalis tubular and autoclave reactors are designed to give the best working efficiency and the wider range of end-use polymers at a very high quality level. Swing plant between LDPE homopolymer & EVA copolymer products is possible through minor modification.

Tubular technology

Polymerization section

The most advanced solutions have been adopted for the reactor configuration, with optimized injection of initiator and gas to ensure high performances and flexibility. The reactor is jacketed by hot pressurized water wherewith the reaction heat is removed. The pressurized hot water system is designed in order to better control the temperature profile, zone by zone, and improve thermal efficiency by low pressure steam generation. The process pressure is smoothly controlled by let-down valve, without pulsating action, with further advantages for stable temperature profile (better quality product) and minor mechanical stress for the reactor.

Product quality

Versalis has a wide range of tubular LDPE products, with MFI ranging from 0,3 to 3,5 g/10' and densities from 0,918 to 0,933 g/cm³. Versalis tubular technology allows to produce grades with narrow molecular weight distribution and thus film grades with excellent optical properties, benchmark in the challenging European Market. The use of oxygen as initiator in combination with peroxide permits to reduce the production costs and improve the product quality with a lower residual solvent content in the polymer.

Autoclave technology

The most advanced solutions have been adopted for the reactor construction, sealing system, connecting system with high pressure piping, stirring motor and related electrical supply under high pressure, stirrer construction, gas initiator injection.

Polymerization section

The polymerization reaction takes place in a multi-zone mixed adiabatic vessel reactor.

The reactor, together with the proprietary designed stirring system, is designed to ensure:

- a wide range of gas repartition, among the multiple gas/initiator injection points;
- the possibility to choose, zone by zone, the right reaction temperature;
- a wide pressure operating conditions which allow to cover the complete product mix, including medium density products.

Energy saving and thermal efficiency are taken into account in the design: a jet pump system is designed to cool down the high pressure separator and the heat of polymerization is partially recovered with low pressure steam generation in high pressure recycle coolers.

Product quality

Versalis has a wide range of autoclave LDPE products with MFI ranging from 0,25 to 200 g/10' and densities from 0,917 to 0,933 g/cm³.

Versalis proprietary design vessel reactor provides a peculiar tree-like branched structure to its products, allowing a competitive approach to application where a proper balance between processability and



mechanical properties is definitely the most important issue, such as injection moulding.

Furthermore, it is well known that a proper grade for extrusion coating application should matches two main issues: a particular melt behavior that enhances the balance between low "neck-in" and high "draw-down" in the extrusion coating and a negligible amount of gels.

Versalis vessel multizone reactor, with its proprietary stirrer design, provides the optimized grade of "back-mixing", giving a peculiar branched structure to the resin. This macromolecular feature provides elasticity to the molten polymer and for this reason autoclave products are generally considered as the most performing for coating application. Autoclave Technology, when equipped with proper process control, can also guaranteed the minimum amount of gels, necessary for film and coating application.

Safety

Safety plays an important role in Versalis plant design. Versalis has developed proprietary designed safety systems to protect the main equipment from ethylene decomposition. The Pyrotechnical Safety System is a proprietary designed safety system developed and successfully installed in currently operating plants. It has been developed to protect autoclave reactor and high pressure separator following an ethylene decomposition. The system is able to react in very few millisecond and to reduce drastically the likelihood for aerial explosion after decomposition events. Versalis pyrotechnical safety system overcomes intrinsic weak points of first generation safety system design. Quench Tower System is designed for tubular technology and it permits to discharge quickly and safely the reactor in case of decomposition event by means of high reliable shutdown logic.

Proprietary process technologies portfolio

Biotech

PROESA® 2G Ethanol and Cellulosic Sugars
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Phenol and derivatives

Cumene (with PBE-1 zeolite based proprietary catalyst)*
Phenol, Acetone, Alphasethylstyrene*
High selectivity Cyclohexanone
Acetone hydrogenation to Isopropyl Alcohol*
Isopropyl Alcohol to Cumene**
Ammoximation (with Titanium silicalite based proprietary catalyst TS-1)

DMC and derivatives

Dimethylcarbonate (via Carbon Monoxide and Methanol)*
Diphenylcarbonate*

Proprietary catalysts

Titanium silicalite
PBE-1 Zeolite
PBE-2 Zeolite

Styrenics

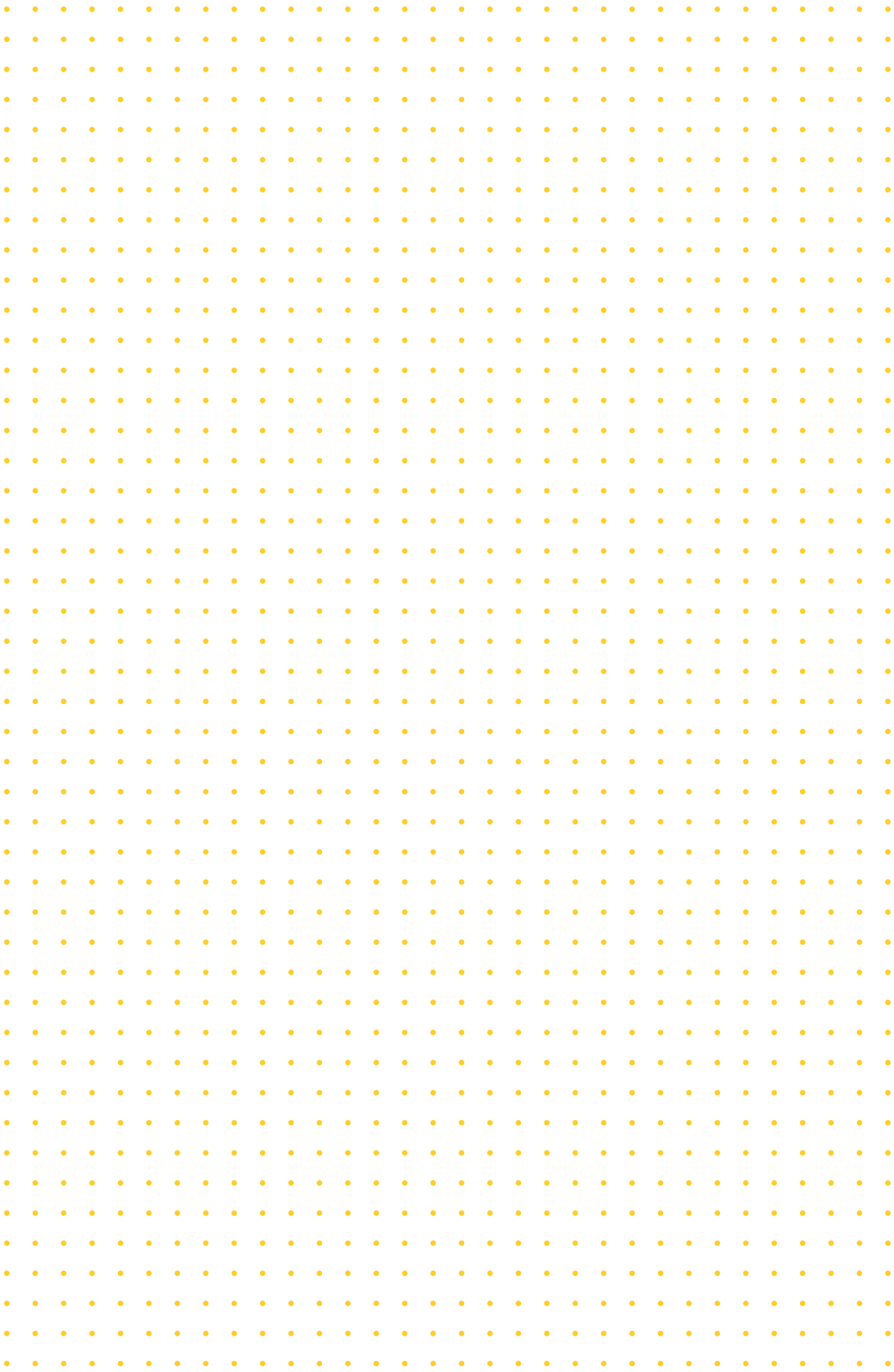
Ethylbenzene (with PBE-1 and PBE-2 zeolite based proprietary catalyst)
Styrene
GPPS
HIPS
EPS suspension polymerization
ABS continuous mass polymerization
SAN

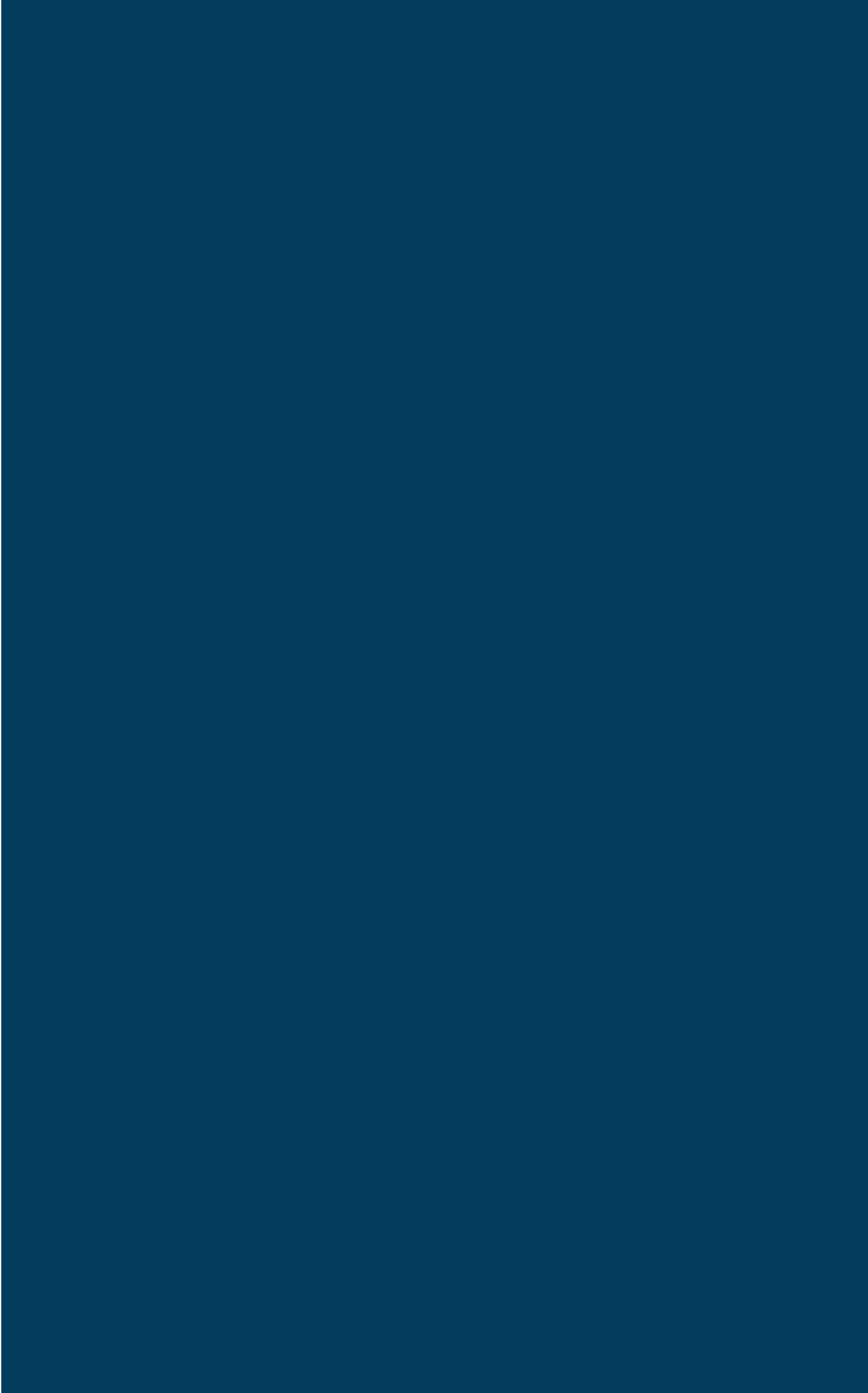
Polyethylene

LDPE
EVA

Elastomers

Emulsion-SBR
HSL Latexes
Solution-SBR
TPR
LCBR
HCBR
NBR
Carboxylated latexes
EP(D)M







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11 - 2018