TOTAL PETROCHEMICALS

REINFORCED PP USING CARBON NANOTUBES NANOSTRUCTURED ELASTOMERIC PP

Marc DUPIRE

TOTAL

Total Petrochemicals
Feluy Research Centre

Total Petrochemicals Research Feluy (Belgium) :
the activities

A R&D centre with a worldwide vocation for the petrochemicals

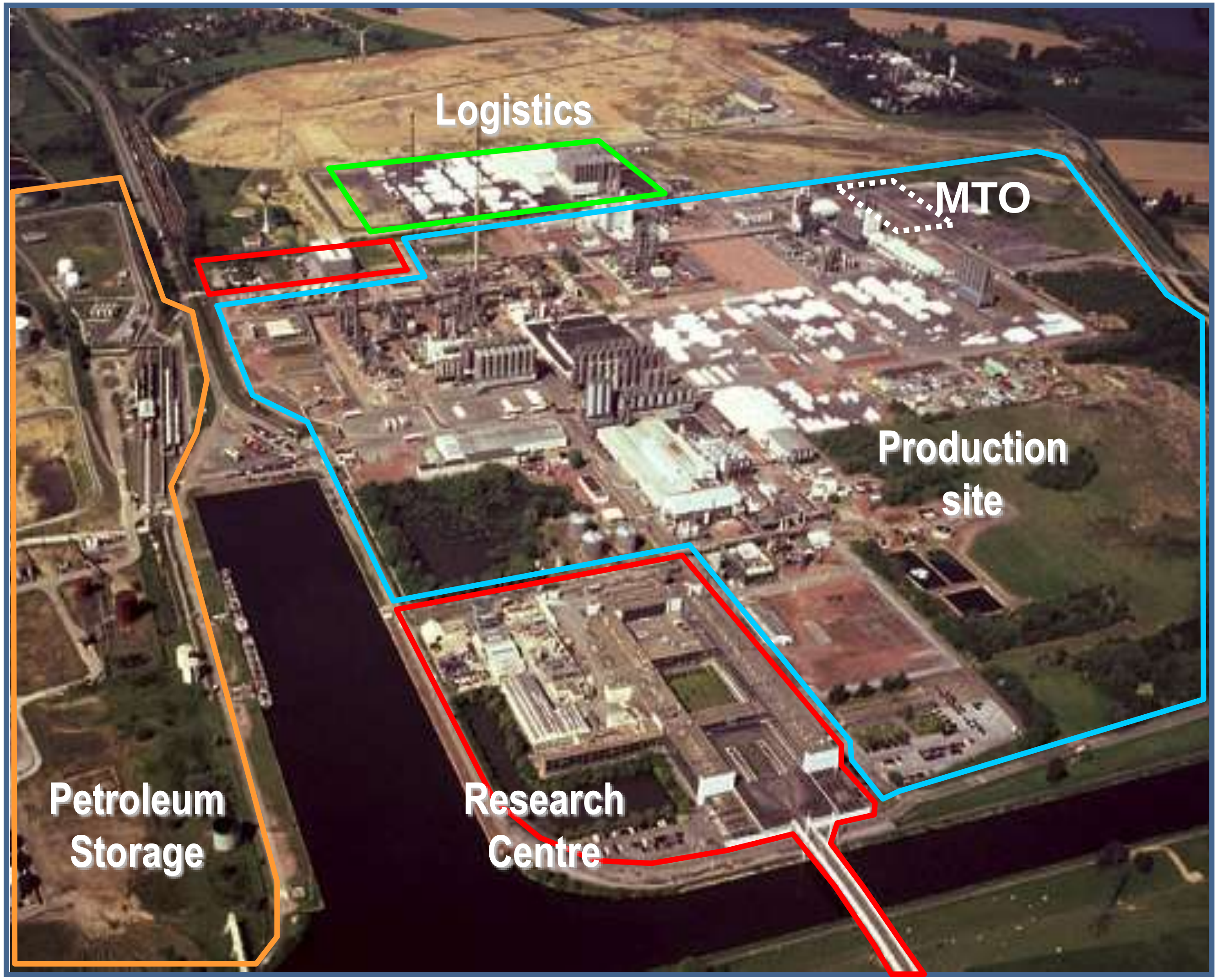
- **Skills and expertise**
  - Applied catalyst research
  - Process developments
  - Product developments
  - Technical site support
  - Technical customer support
- **A catalyst team for Base Chemicals & Refining**
- **An integrated Polyolefins team « from catalyst to customer »**
- **Worldwide support teams for petrochemicals**

R&D polyolefins :
accompany and anticipate the market

All the competences together on the same site

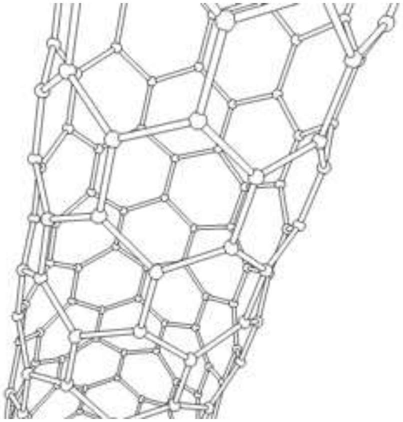
- **A concentrated team for technical assistance of Customers**
  - Actively monitoring the market
- **For development of new products**
  - An expertise in Catalysts and high throughput screening
  - A « continuous » PE/PP pilot plant for scaling-up purposes
  - « Semi-industrial » equipments for transformation
- **A team of process specialists for site support**
- **The programmes**
  - To reduce costs of catalysts and products
  - To optimise industrial units
  - To develop high margin technical products
  - To take our market shares in biopolymers

Total Petrochemicals in Feluy (Belgium) :
a successful growth …



100 hectares of petrochemical activity, outside urban zones, close to the markets

TOTAL



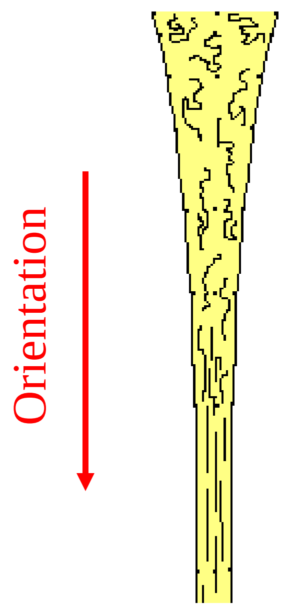
REINFORCED POLYOLEFINS USING CARBON NANOTUBES

Polypropylene

- PP Current material (Isotropic or slightly oriented) ⇒ E modulus : 1.3 – 2 GPa

How to improve mechanical properties ?

1. Increase molecular orientation (strong effect : PP is a polymer that can easily be oriented)



Orientation	E modulus (GPa)	Tensile strength (MPa)
Isotropic material	1.5	30 – 40
Injection molding	2.0	40
Special injection techniques	4 – 5	100 – 120
Melt spinning	4 – 5	100 – 400
Melt spinning + drawing	10 – 20	400 – 1200
Gel spinning	40	1200 – 1500
Theoretical max	40 - 80	1800

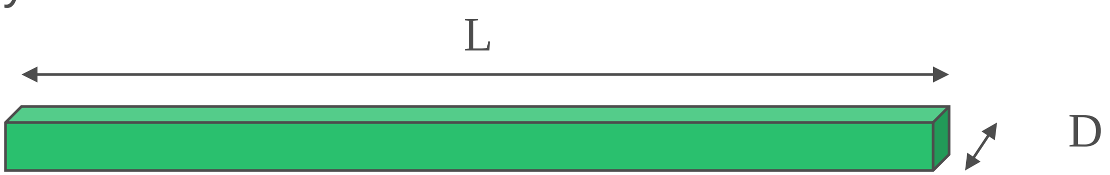
2. Introduce reinforcement agents (high rigidity dispersed phase)

TOTAL

Reinforcement agents

Conditions for an efficient reinforcement :

- Highest possible rigidity
- Highest possible aspect ratio L/D
- Orientation of long axis L as close as possible to tensile axis
- Good adhesion to the polymer matrix
- Good dispersion



Composite stiffness E_c

$$E_c = f_0 \, f_l \, E_f \, \Phi_f + E_m \, \Phi_m$$

with

f_0 : orientation efficiency factor

f_l : effect of fiber length (aspect ratio)

E_f and E_m : moduli of filler and matrix

Φ_f and Φ_m : volume fractions of filler and matrix

Types of reinforcement agents

Classical "microscopic" fillers (talc, mica, chalk, ..) (Sizeable improvement for high loadings 30-40wt%)

E modulus : Talc 3.8 GPa

Short glass and Carbon fibers (L~ 0.5 mm; D~17 µm)(injection molding)

E modulus : 5 - 7 GPa

Short fibers with high aspect ratio (L~ 5 mm before processing; D ~ 17 µm) (pultrusion)

E modulus : 10 GPa

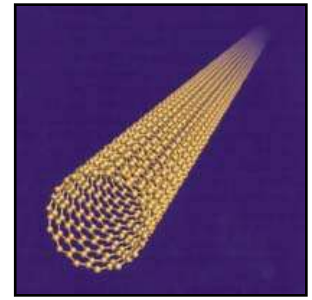
Continuous long fibers (Carbon fibers, polyaramid, ..)

E modulus : up to 20 GPa

Ultimate tensile strength : up to 350 MPa

Orientation	E modulus (GPa)	Tensile strength (MPa)
Isotropic material	1.5	30 – 40
Injection molding	2.0	40
Special injection techniques	4 – 5	100 – 120
Melt spinning	4 – 5	100 – 400
Melt spinning + drawing	10 – 20	400 – 1200
Gel spinning	40	1200 – 1500
Theoretical max	40 - 80	1800

NEW REINFORCEMENT MATERIAL : CARBON NANOTUBES

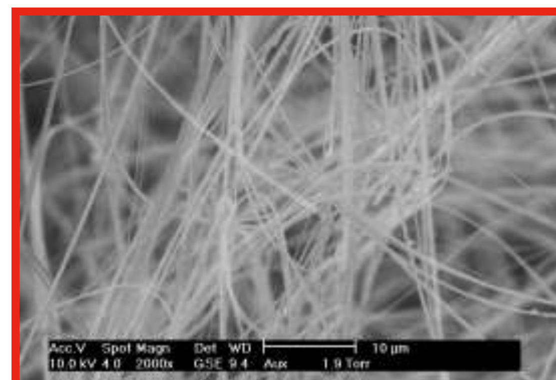


Nanotubes : promising characteristics

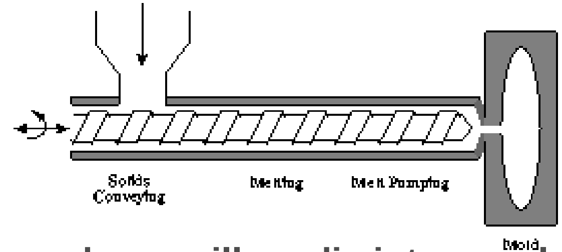
- Huge rigidity (≥ 1000 GPa)
- Huge tenacity : 150 – 200 GPa (40 times that of C fibers)
- High L/D ratio (≥ 1000 !)
- Flexible and strong (able to be processed using conventional processing techniques for polymers without loss of aspect ratio)

Possible hindrances

- High entanglement (limits orientation and homogeneous dispersion)
- Limited compatibility with polyolefins
- Black color
- Still high price and limited availability
- Best reinforcement performance in polar polymers (PVOH, PA, …) at low loadings



ORIENTATION PROCESSES : INJECTION MOLDING

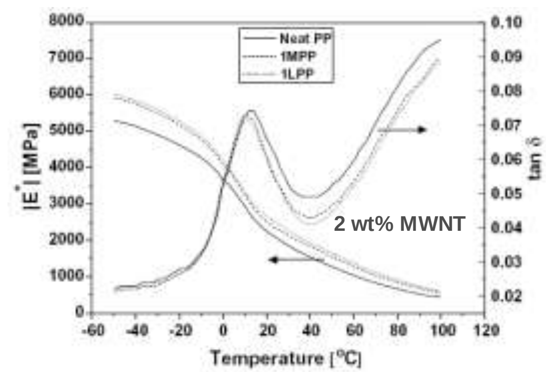


- **Principle :**
  The molten polymer is injected under high pressure through a capillary die into a mold, imparting some orientation to the matrix

- **Results**

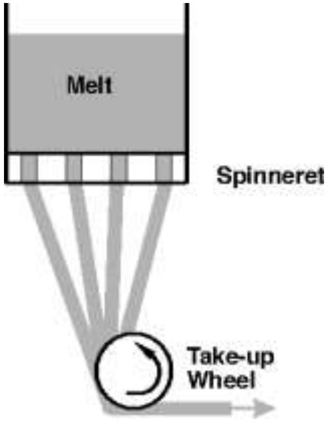
Material	E modulus (MPa)	Relative improvement (%)	Ultimate tensile strength (MPa)	Relative improvement (%)
Neat PP	1400	0	39.2	0
PP + 4 wt% CNT	1820	30	41.7	6
PP + 10 wt% CNT	1920	37	45.1	15

- **Conclusions**
  Very limited improvement (confirmed by other publications)
  Possible reasons :
  - negligible orientation
  - poor dispersion / aggregates
  - microvoids- poor wetting of fibers



H. Zhang & al., Europ. Polym. J., 43, 3197 (2007)

ORIENTATION PROCESSES : MELT SPINNING



- **Principle :**
  The molten polymer is pushed through a capillary die at high speed (100 m/min) and the molten filament is drawn out on a rotating wheel

- **Results**

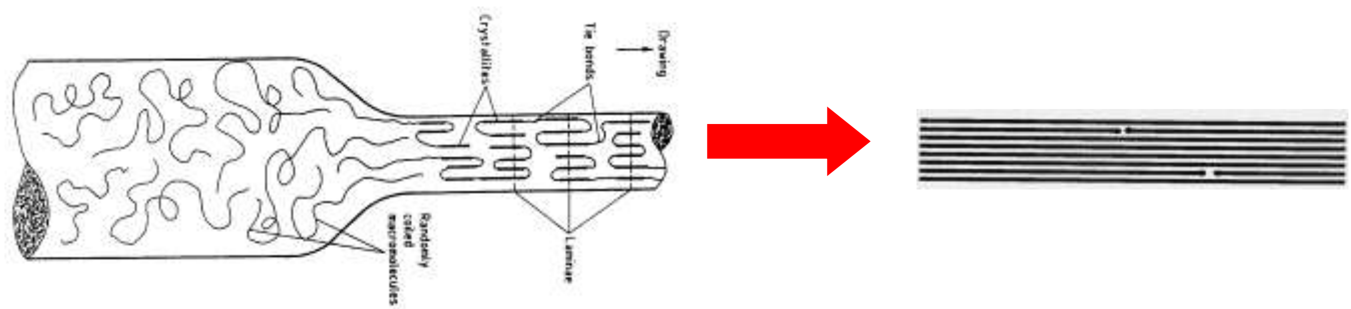
Material 40 µm fibers	Tenacity (MPa)	Elongation at break (%)
Neat PP	103	600
PP + 3 wt% CNT	95	500

- **Conclusions**
  - As for injection molding, limited or no improvement
  - Could be improved by higher haul-off speed but spin line stress too low for sufficient alignment of C nanotubes (fiber breakage occurs before that event)

COLD DRAWING

- **Observation**
  The orientation imparted to C nanotubes using conventional melt processing is too low and the resulting mechanical properties are not interesting

- **Reason for this poor result**
  Too low stress imposed on nanotubes resulting from the low viscosity of the matrix and the high entanglement of the tubes



- **Improvement**
  Additional cold drawing (at temperatures above the polymer glass transition temperature and below its melting temperature) of the composite $\Rightarrow$ stronger orientation of the polymer crystals and macromolecules $\Rightarrow$ disentanglement and orientation of C nanotubes

ORIENTATION PROCESSES
FIBER MELT SPINNING WITH SOLID STATE DRAWING

- **Principle :**
  The fibers are subsequently drawn at 110 °C with different stretching ratios at a rate of 10%/min (polymer orientation measured via birefringence)

- **Results**

Stretching ratio : 2.5

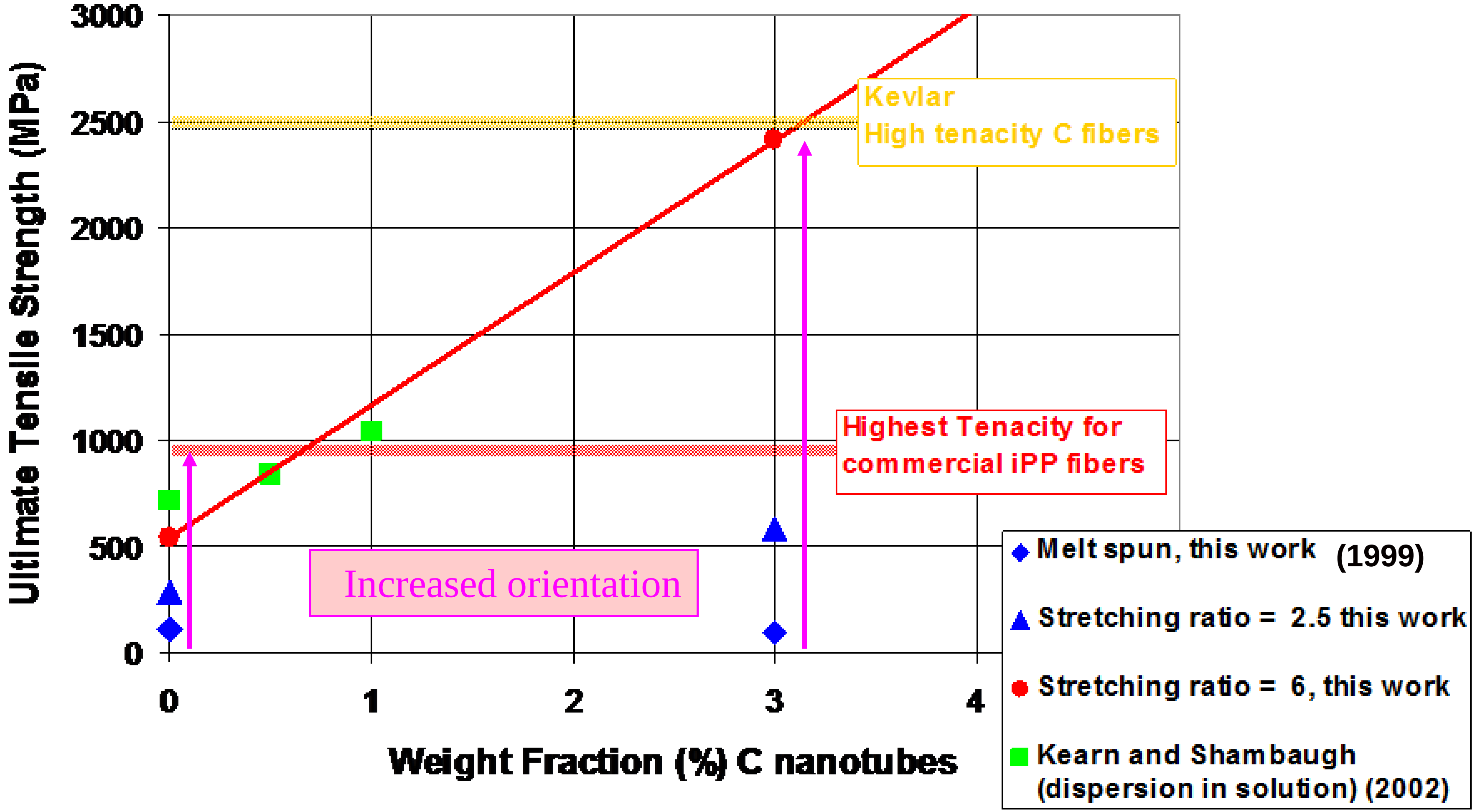
Material (~ 20 µm fibers)	E modulus 4% (GPa)	Tenacity (MPa)	Elongation at break (%)
Neat PP	2.3	285	60
PP + 3wt% C black	2.5	252	75
PP + 3 wt% CNT	6.3	585	47

Stretching ratio : 6.5

Material (~ 7 µm fibers)	E modulus 4% (GPa)	Tenacity (MPa)	Elongation at break (%)
Neat PP	5.2	540	27
PP + 3wt% C black	5.2	549	27
PP + 3 wt% CNT	17.1	2410	20

- **Proprietary technology (US 6,331,265 ; Priority date 1999)**

TENACITY OF C NANOTUBES-REINFORCED IPP FIBERS

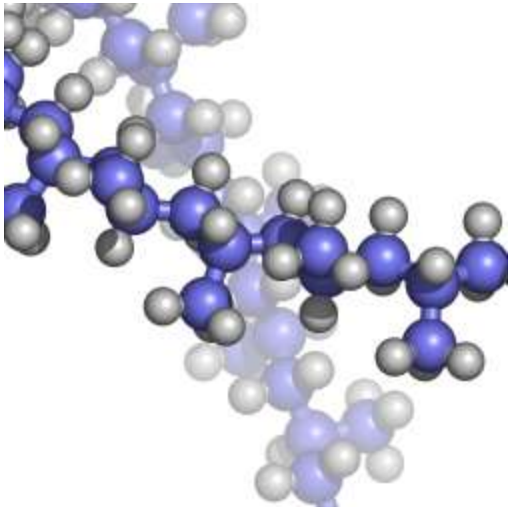


CONCLUSIONS

- **The mechanical properties of polypropylene fibers are significantly enhanced with the addition of a small amount (3 wt%) of Carbon nanotube provided a sufficient orientation is obtained :**
    - Very high tenacity : +350% compared to neat PP (ultimate tensile strength greater than the value predicted for 100% crystalline iPP)
    - High E modulus : + 230% compared to neat PP (better than high tenacity PP fibers)

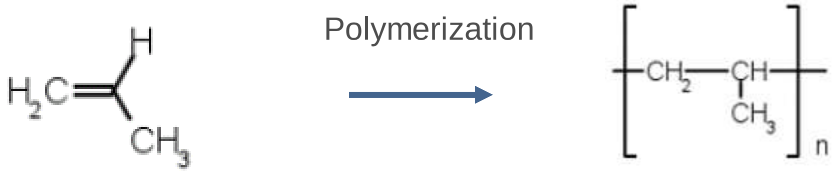
- **This result could still be improved by increasing the nanotubes loading and optimizing the orientation process, leading to high performance fibers.**

- **The required orientation has been achieved using a 2-step process :**
    - Melt processing with low orientation
    - Solid state drawing (much more efficient than in melt state)

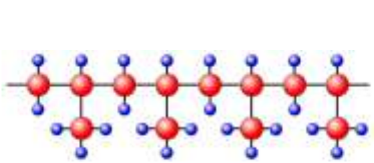


NANOSTRUCTURED ELASTOMERIC PP

Polypropylene

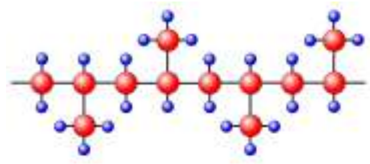


3 stereo-isomers :



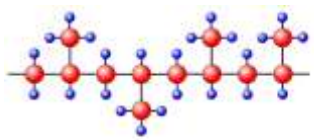
Isotactic PP

iPP



Syndiotactic PP

sPP



Atactic PP

aPP

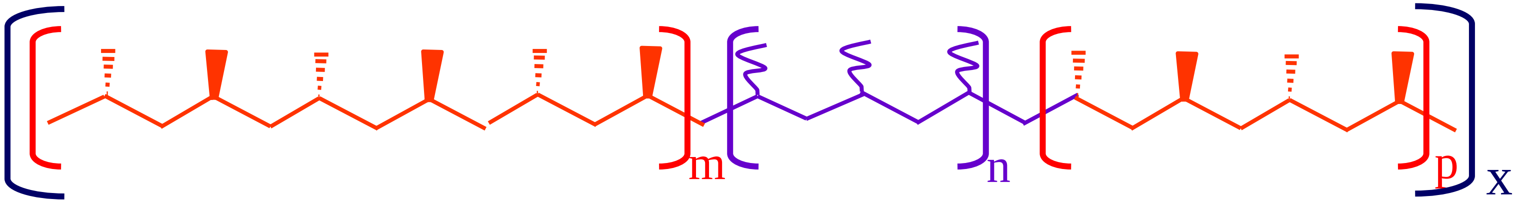
Semi-crystalline

Amorphous

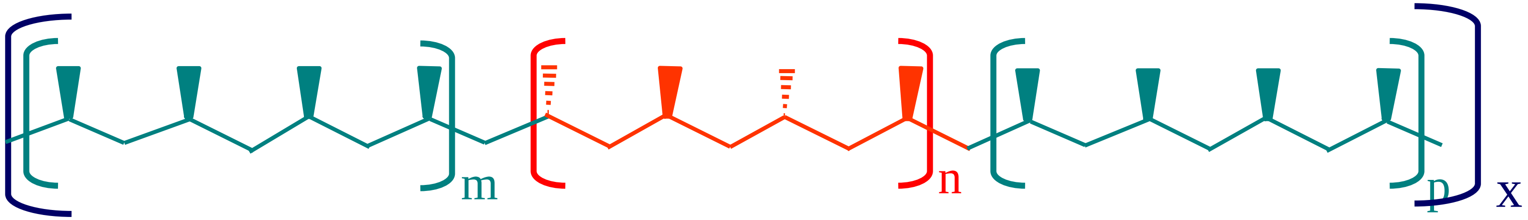
Stereoblock PP

- New type of propylene homopolymer having a chemical structure consisting of blocks of different microtacticities regularly alternating. It results from a changing stereocontrol during polymerization

- Syndiotactic - atactic PP : s-aPP



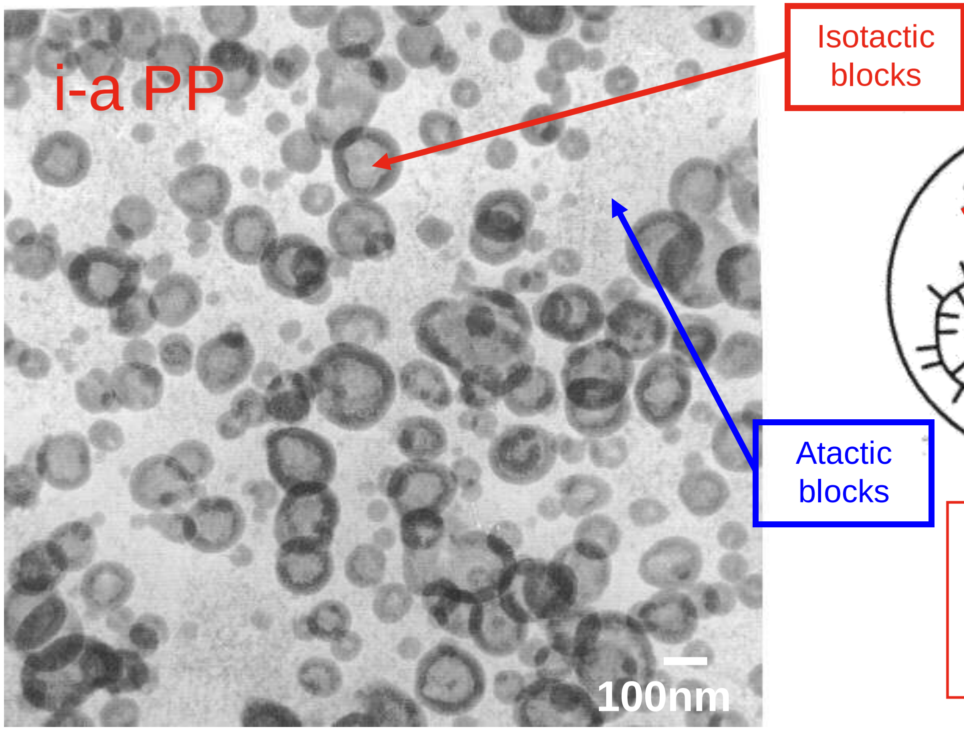
- Isotactic - syndio PP : i-sPP

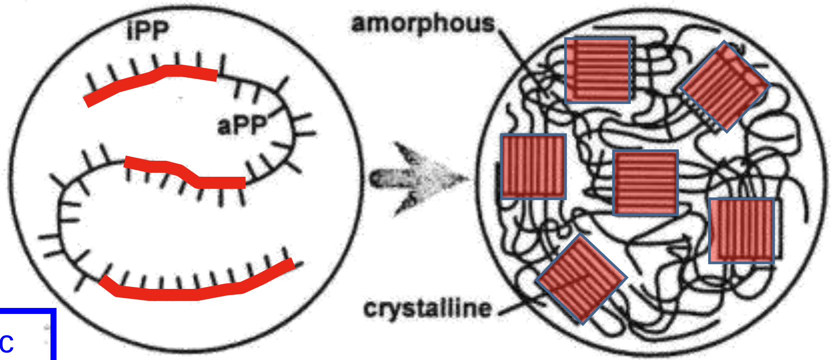


- Proprietary technology (WO 98/02469 - EP 747406)
  - Original structure obtained by polymerization using specific metallocene catalysts
  - Low pressure solution process (light solvents)

Self-ordering structures

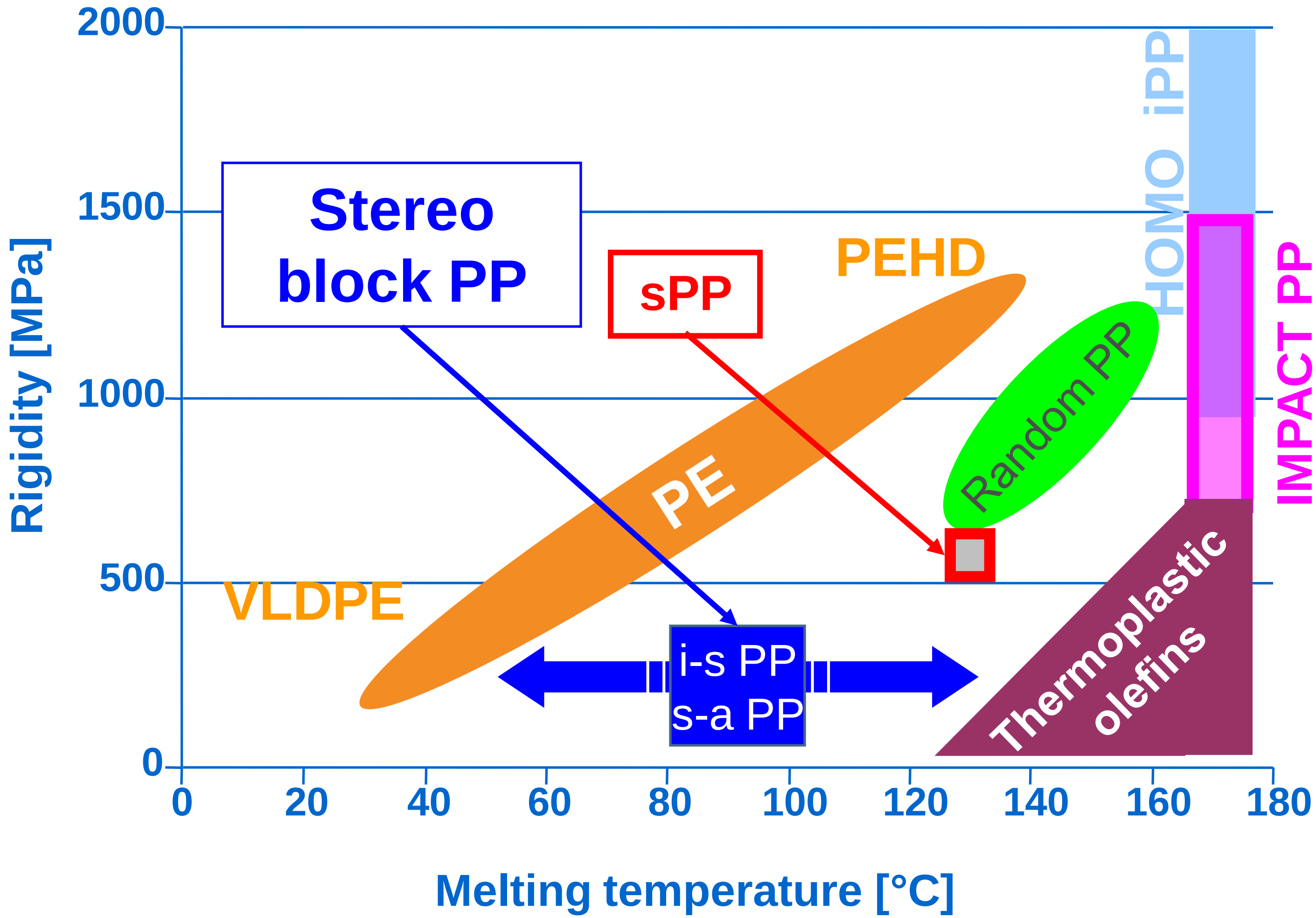
- These polymer chains with regularly alternating sequences of controlled stereotacticities are less crystallizable than conventional PP homopolymers.
- As sPP, iPP and aPP are immiscible, these stereoblock PP behave differently from conventional PP homopolymers
- Nanostructuration : self-ordering with long range order and nanodomains





Brand new elastomeric material with original structures and properties

ELASTOMERIC PP



Typical properties

Properties	Units	i-s PP	s-a PP
Molar Weight	kDa	50 - 300	50 - 300
Molar Weight Distribution		2 – 3.5	2 – 3.5
Iso-blocks length	Units	12 to 16	
Syndio-blocks length	Units	5 to 7	10 to 24
aPP	%		9 to 27
Melting temperature Tm	°C	80 – 90	100 - 135
Glass transition temperature Tg	°C	~ 0	~ 0
Young’s Modulus	MPa	50 - 400	10 – 300
Elongation at break	%	Up to 1000	Up to 1000
Impact strength at 23°C	kJ/m²	50 to no break	No break
Impact strength at -20°C	kJ/m²	~ 2	~ 2

Conclusions

Stereoblock PP are original materials with original structure and properties :

- They are homopolymer PP produced using proprietary single-site metallocene catalysis
- The backbone consists of blocks of different tacticities resulting from regularly alternating the monomer stereo-insertion in the growing chain
- Self-ordering with long range order and nanodomains can be observed
- They behave differently from conventional homopolymer PP , like thermoplastic elastomers