AIMPLAS
PLASTICS TECHNOLOGY
CENTRE

AIMPLAS
EXCELLENCE IN PLASTIC

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PLASTICS TECHNOLOGY
CENTRE

Development of polymerization processes

25TH EDITION
EUBCE 2017
European Biomass Conference & Exhibition

12-15 JUNE | STOCKHOLM SWEDEN
Stockholmsmässan

Dr. Amador García Sancho

bioREFINE-2G

SEVENTH FRAMEWORK PROGRAMME

Follow AIMPLAS

Outline

- AIMPLAS
- Polymerization methods
  - Fumaric based
  - Glutaric based
- Characterization
- Summary

What is AIMPLAS?

AIMPLAS is a **Technology Centre** with more than 25 years of experience in the plastic sector

Staff

Formed by a team of more than 125 highly qualified professionals

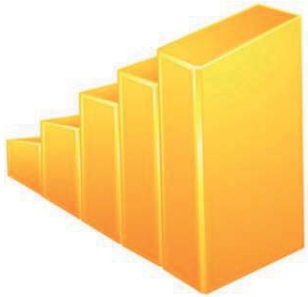
64% women· **36%** men · **39 years** average age · **16** PhD

Resources

Over 9,000 m^2 facilities with the cutting-edge technology

See video

Our greatest asset: **your confidence**



€ 8.4M
revenues

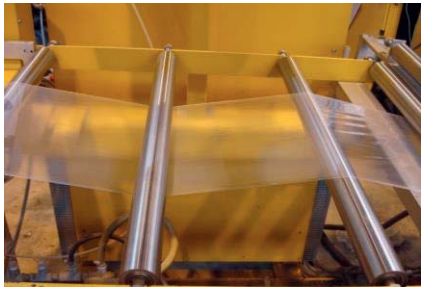
+2,300
customers

+574
associated companies

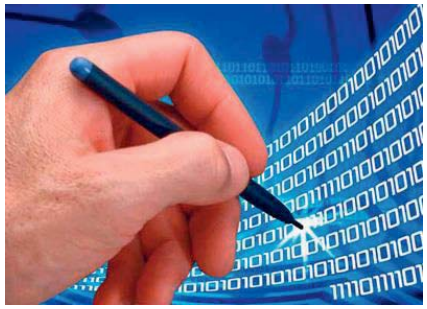
2016 DATA

70% of incomes from R+D projects.
120 projects (32 EU ongoing projects)

Solutions for Plastics



- R&D&Innovation projects
- Analysis and testing
- Polymer synthesis
- Material processing
- Technical assessment
- Competitive intelligence
- Training



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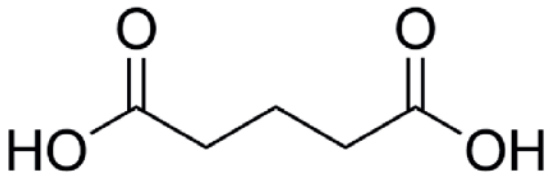
Polymerization methods

Grant Agreement nº 613771

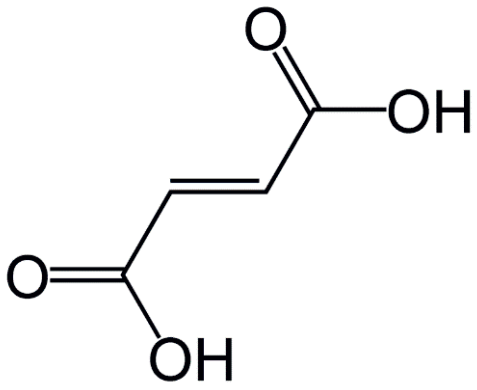
Goal

BioREFINE-2G project

Develop polymerization methods employing:



Glutaric acid



Fumaric acid

Business opportunities in polymer sector

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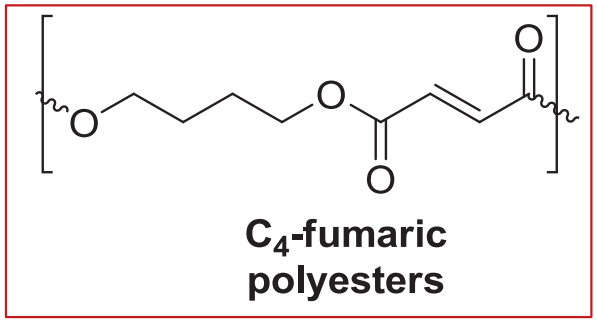
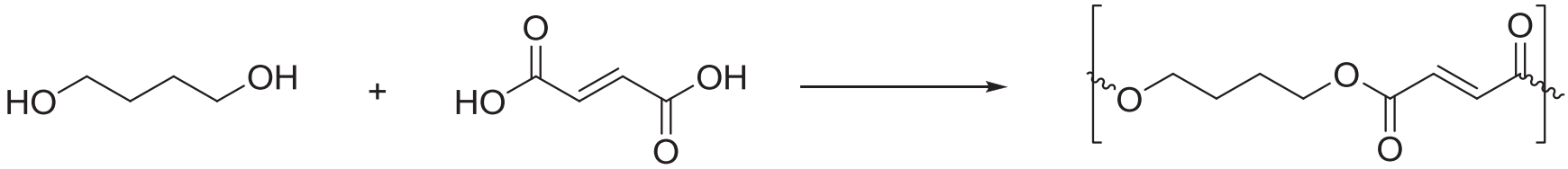
Polymerization methods: fumaric

Polymerization methods: Fumaric

Target compound



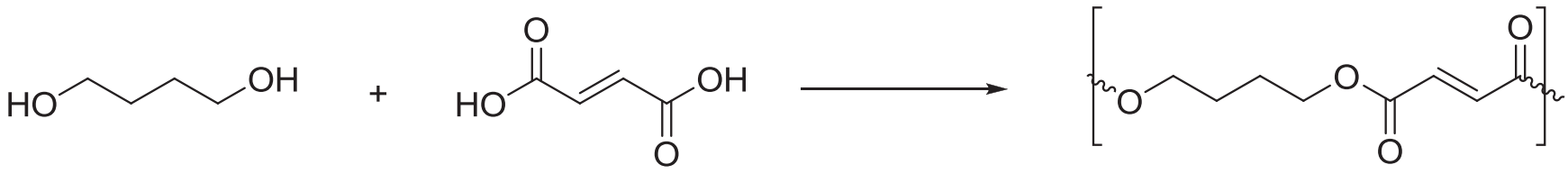
C_4-fumaric polyesters



1,4-butanediol **fumaric acid** **C_4-fumaric polyesters**

Polymerization methods: Fumaric and biofumaric

- Exploring the reactivity of commercial fumaric



1,4-butanediol **fumaric acid** **C_4-fumaric polyesters**

Temperatures: 160-165ºC

No crosslinking (double bound is detected)

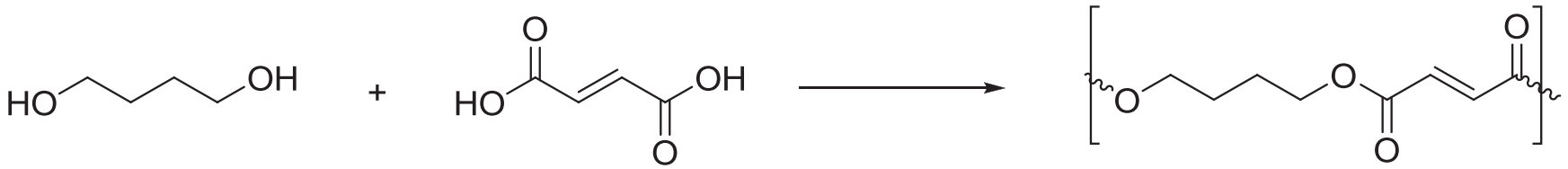
Inhibitors (hydroquinone)

Thermoplastic material

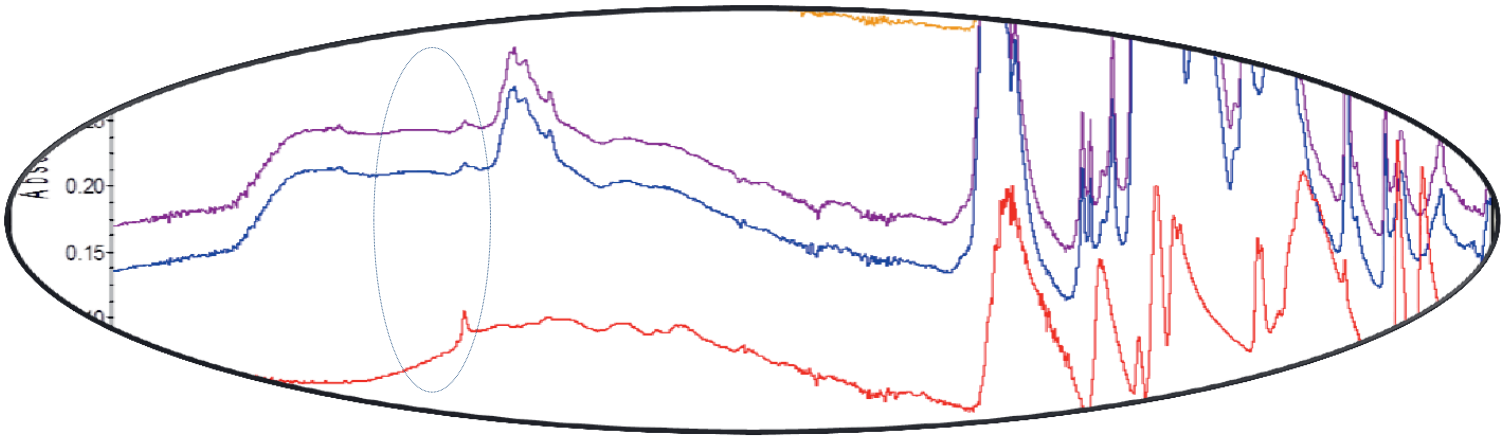
Nat Protoc**. 2009** ; 4(4): 518–525. doi:10.1038/nprot.2009.24.

Polymerization methods: Fumaric and biofumaric

- Exploring the reactivity of commercial fumaric



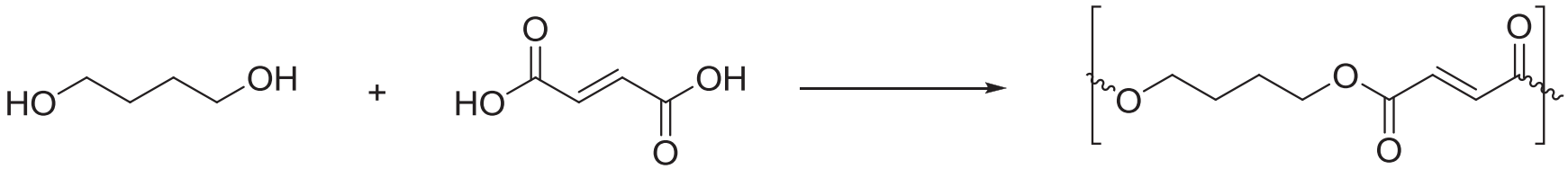
1,4-butanediol **fumaric acid** **C_4-fumaric polyesters**



Nat Protoc. **2009** ; 4(4): 518–525. doi:10.1038/nprot.2009.24.

Polymerization methods: Fumaric and biofumaric

- Exploring the reactivity of **bio-fumaric:**



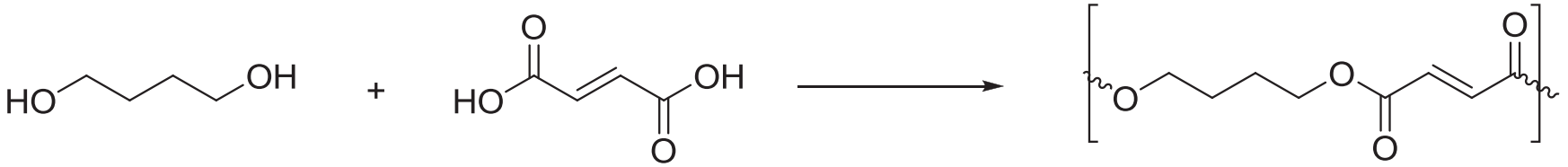
1,4-butanediol **bio-fumaric acid** **C_4-fumaric bio-polyesters**

biotrend

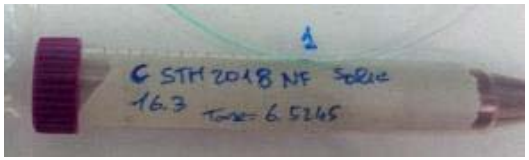
Inovação e engenharia em biotecnologia

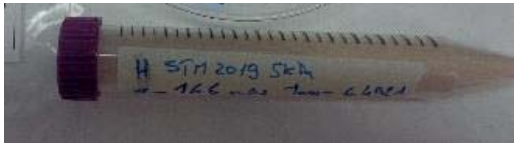
Polymerization methods: Fumaric and biofumaric

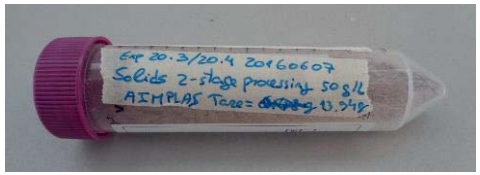
- Exploring the reactivity of bio-fumaric by:



1,4-butanediol **bio-fumaric acid** **C_4-fumaric bio-polyesters**

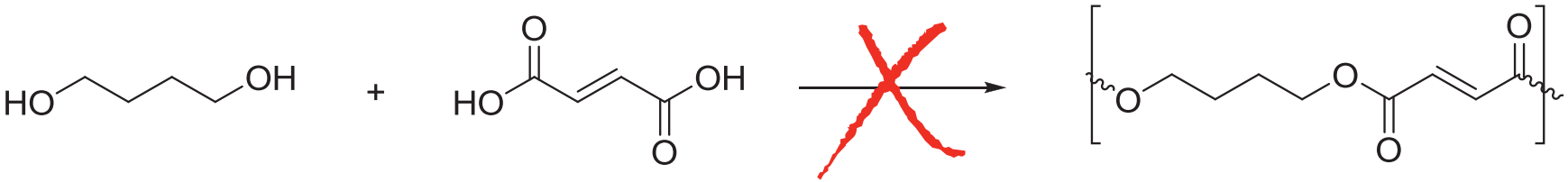




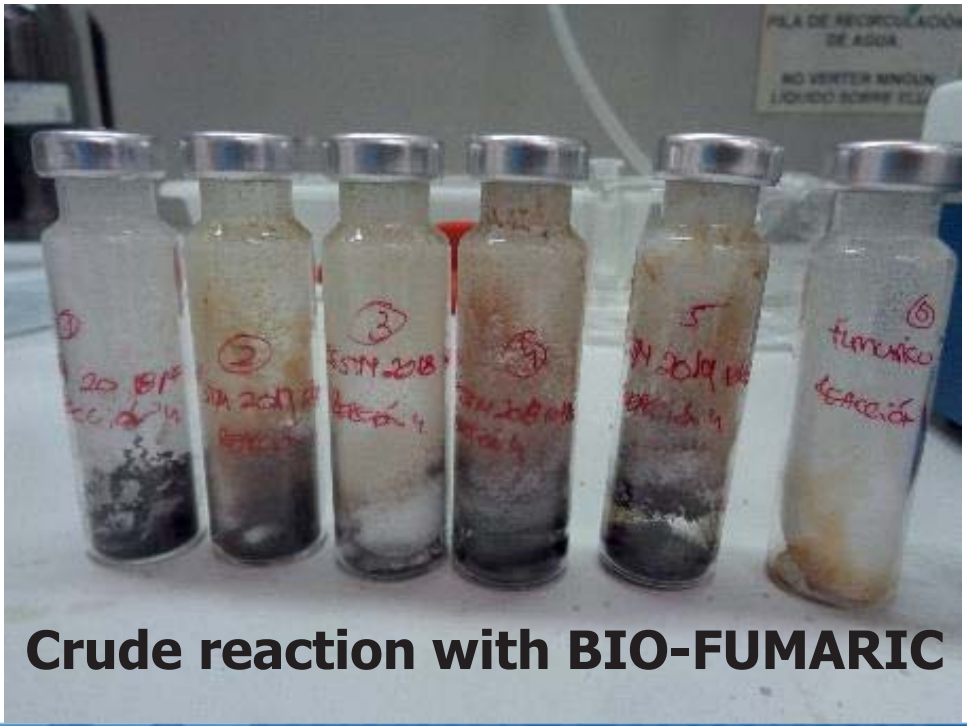


Reactivity of fumaric and biofumaric acid

- Exploring the reactivity of bio-fumaric by:



1,4-butanediol **bio-fumaric acid** **C_4-fumaric bio-polyesters**



Crude reaction with BIO-FUMARIC

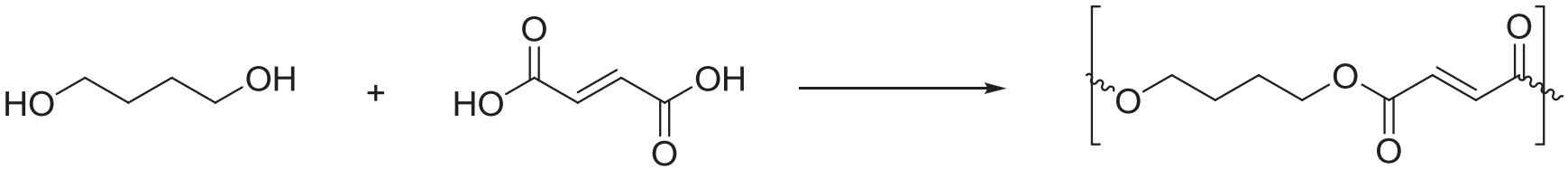
Temperatures: 160-165ºC

Polymerization fails/No reaction occurs

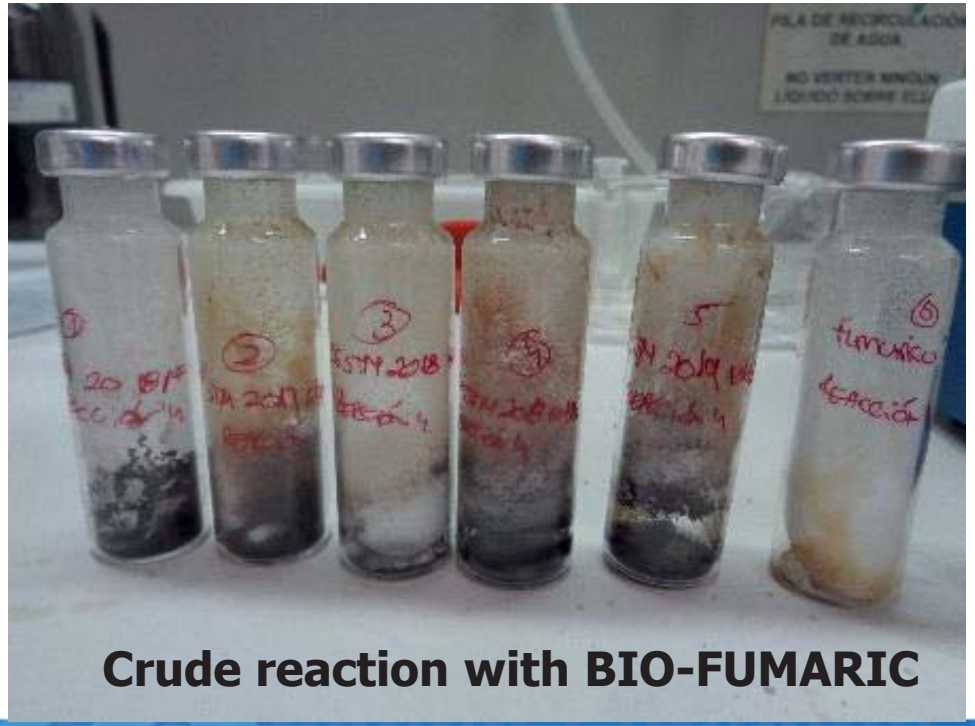
Inhibitors (hydroquinone) and free of inh.

Polymerization methods: Fumaric and biofumaric

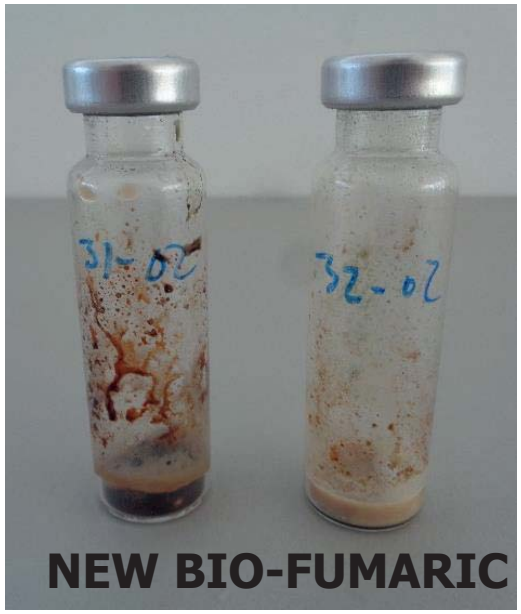
- Exploring the reactivity of bio-fumaric by:



1,4-butanediol **bio-fumaric acid** **C_4-fumaric bio-polyesters**



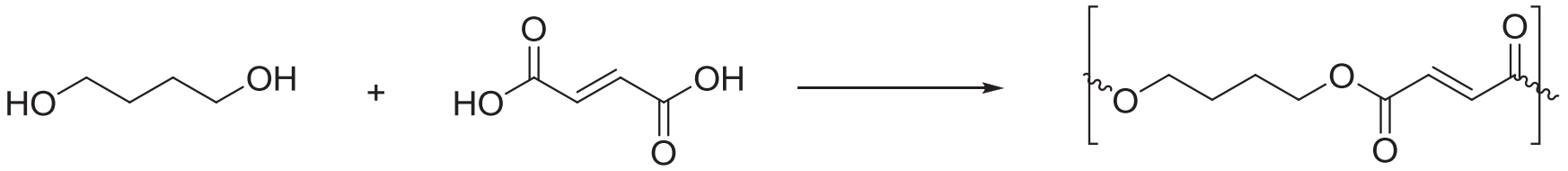
Crude reaction with BIO-FUMARIC



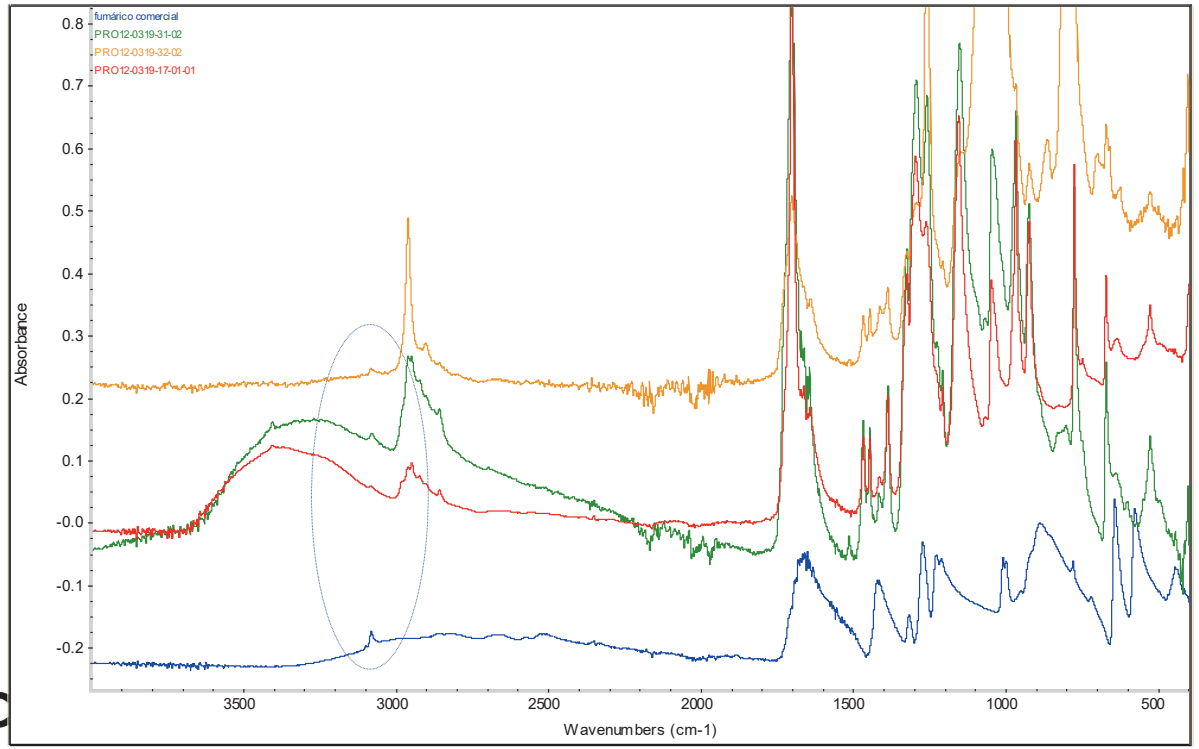
NEW BIO-FUMARIC

Polymerization methods: Fumaric and biofumaric

- Exploring the reactivity of bio-fumaric by:



1,4-butanediol **bio-fumaric acid** **C_4-fumaric bio-polyesters**



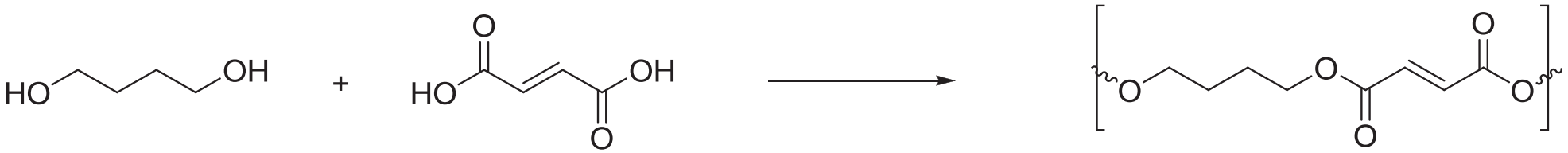
NEW GRADES BIO-FUMARIC

Polymerization methods: Fumaric and biofumaric

1,4-butanediol **fumaric acid** **C_4-fumaric bio-polyesters**

AIMPLAS Reference:	Fumaric Source: BIOTREND	T[a]	Catalyst+Inhbitor	Polymerization
PRO12-0319-22-01	H F STM 2019 5KDa	160-165	DBTDL+Hydroquinone	✗
PRO12-0319-31	**exp 20.3/20.4 20160607 solids 2-stage processing 50g/L**	**160-165**	**DBTDL+Hydroquinone**	✓
PRO12-0319-32	**exp 21.17.1 + 21.17.2 20160720 solid recovery final step**	**160-165**	**DBTDL+Hydroquinone**	✓

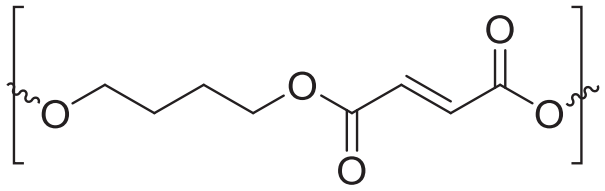
Polymerization methods: Fumaric and biofumaric



1,4-butanediol | fumaric acid | C_4-fumaric bio-polyesters

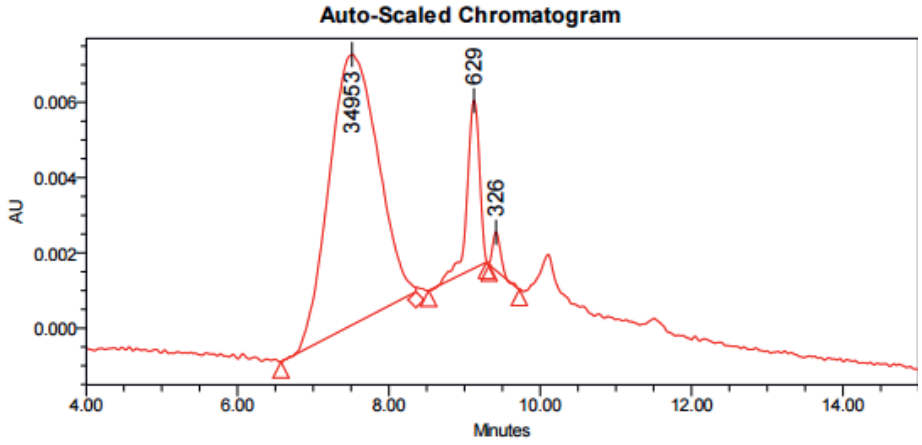
AIMPLAS Reference:	Fumaric Source: BIOTREND	T^a	Catalyst+Inhbitor	Polymerization
PRO12-0319-39	Biotrend 20170306	160-165	ZnCl2+Hydroquinone	✓

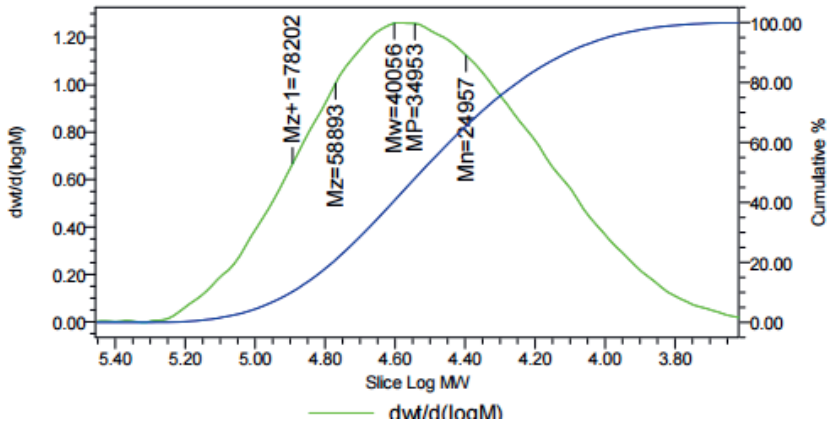
Polymerization methods: Fumaric and biofumaric



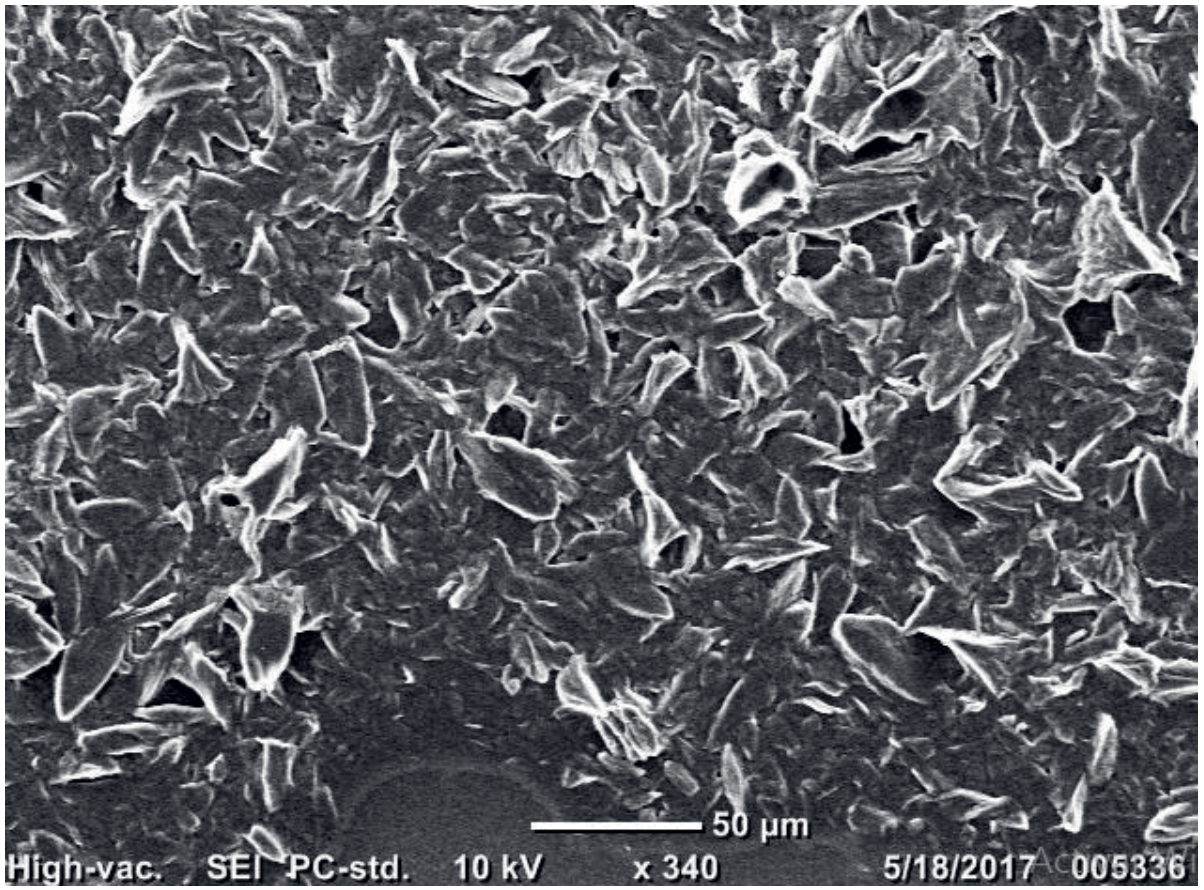
C_4-fumaric
bio-polyesters

AIMPLAS Reference:	Fumaric Source: BIOTREND
PRO12-0319-39	Biotrend 20170306





Polymerization methods: Fumaric and biofumaric



Membranes for tissue engineering in biomedical sector

Polymerization methods: Fumaric and biofumaric

- ✓ Polymerization of fumaric and biofumaric acid have been optimized.
- ✓ BIOTREND has optimized the biofumaric purification.
- ✓ New biopolyester derived from biofumaric acid have been developed for biomedical aplications.

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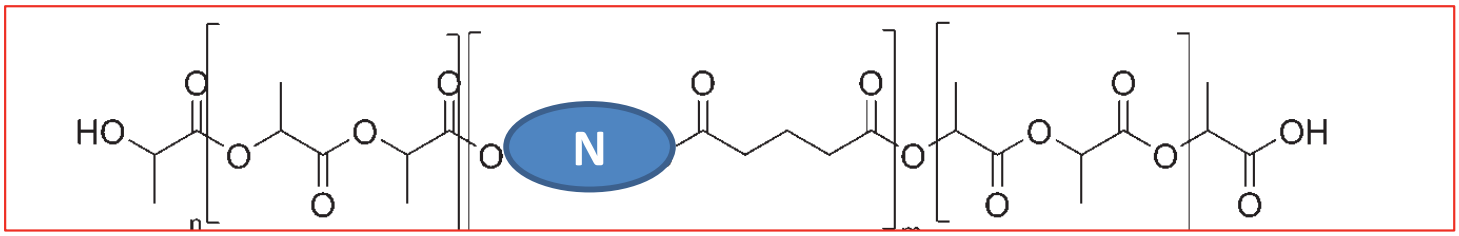
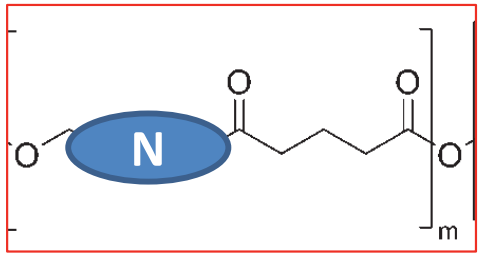
Polymerization methods: glutaric

Polymerization methods: PLA-glutaric copolymers.

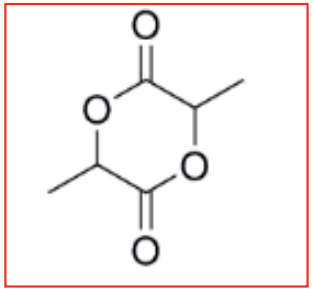


PLA-Glutaric Copolymers



Glutaric Copolymers

+



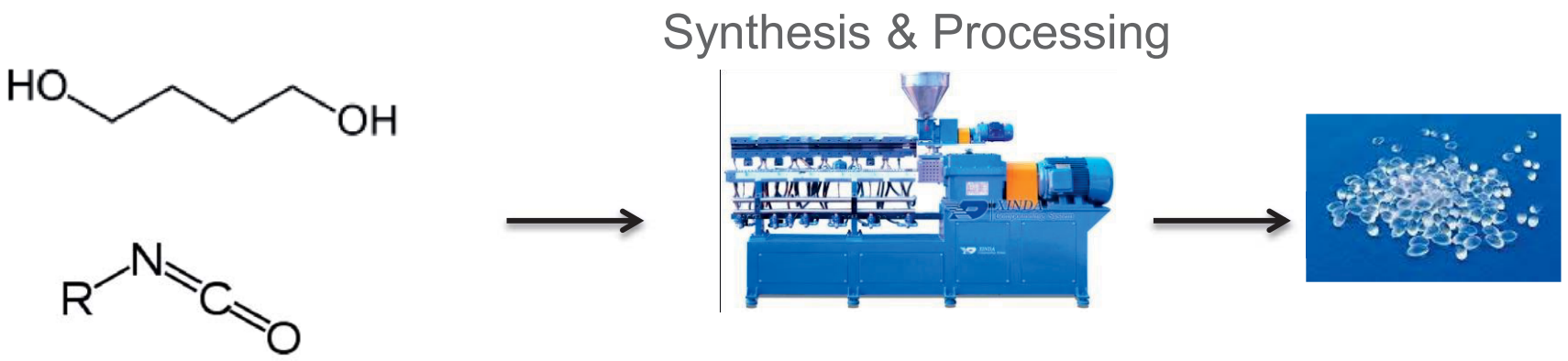
Lactide

Polymerization methods: PLA-glutaric copolymers.

Polymerization methods: PLA-glutaric copolymers.

Reactive extrusion.

REX is a manufacturing method that combines the traditionally separated chemical process (polymer synthesis and/or modification) and extrusion (melting, blending, structuring, de-volatilization and shaping)



Lambla, M.; Macromolecular Symposia **1994**, *83,* 37-48

Polymerization methods: PLA-glutaric copolymers.

Reactive extrusion.

-Free solvent process.

-Fast process (3-10 minutes synthesis is carried out)

-Better management of high viscose products.

-Water can be removed due high temperature and devolatilization.

-Requires previous knowledge of polymerization reaction in solution.

Polymerization methods: PLA-glutaric copolymers.

Leistritz ZSE 27 MAXX co-rotating twin screw extruder

14 modules

27 mm of screw diameter

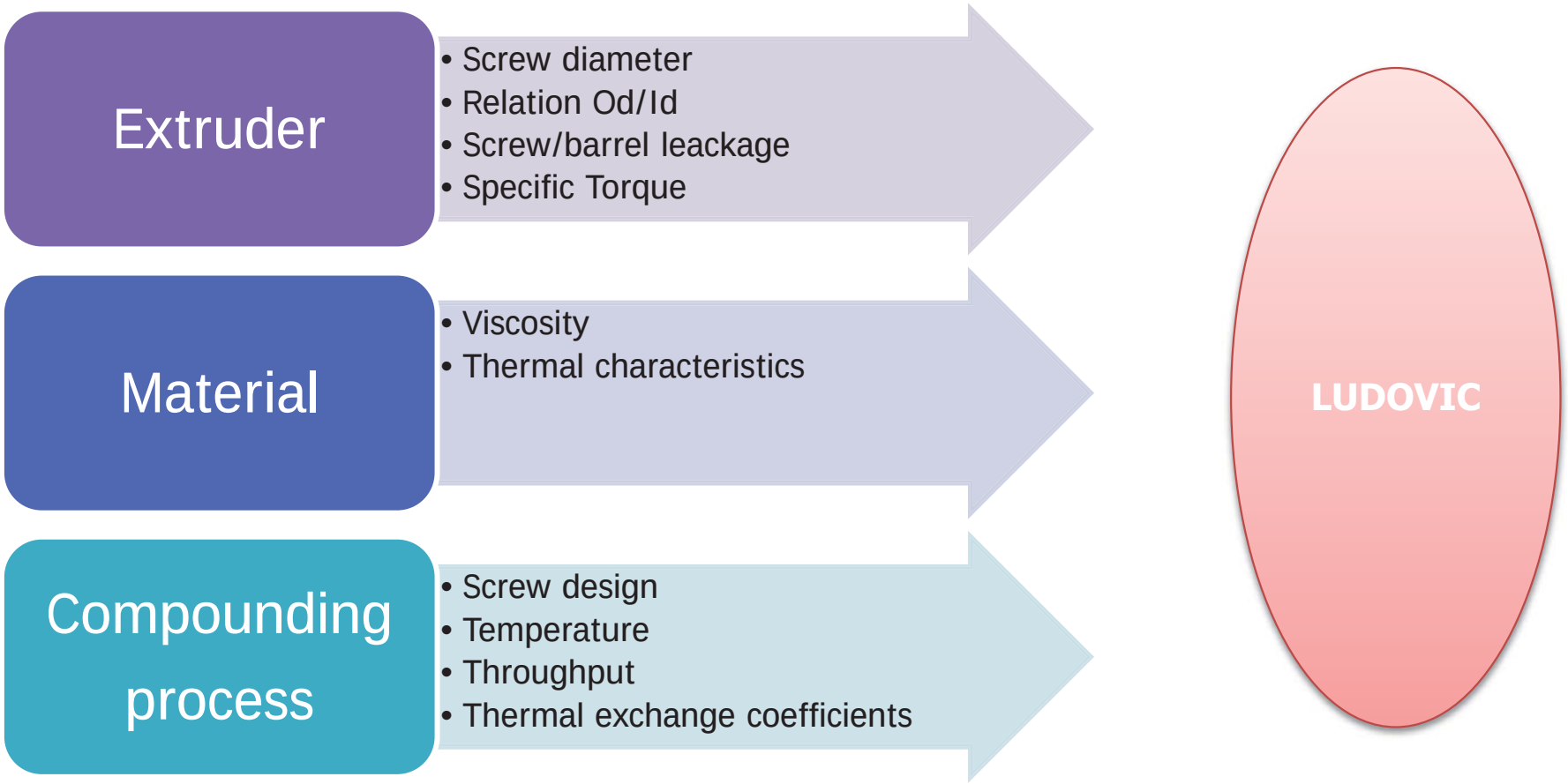
L/D 56 to achieve higher residence time

Polymerization methods: PLA-glutaric copolymers.

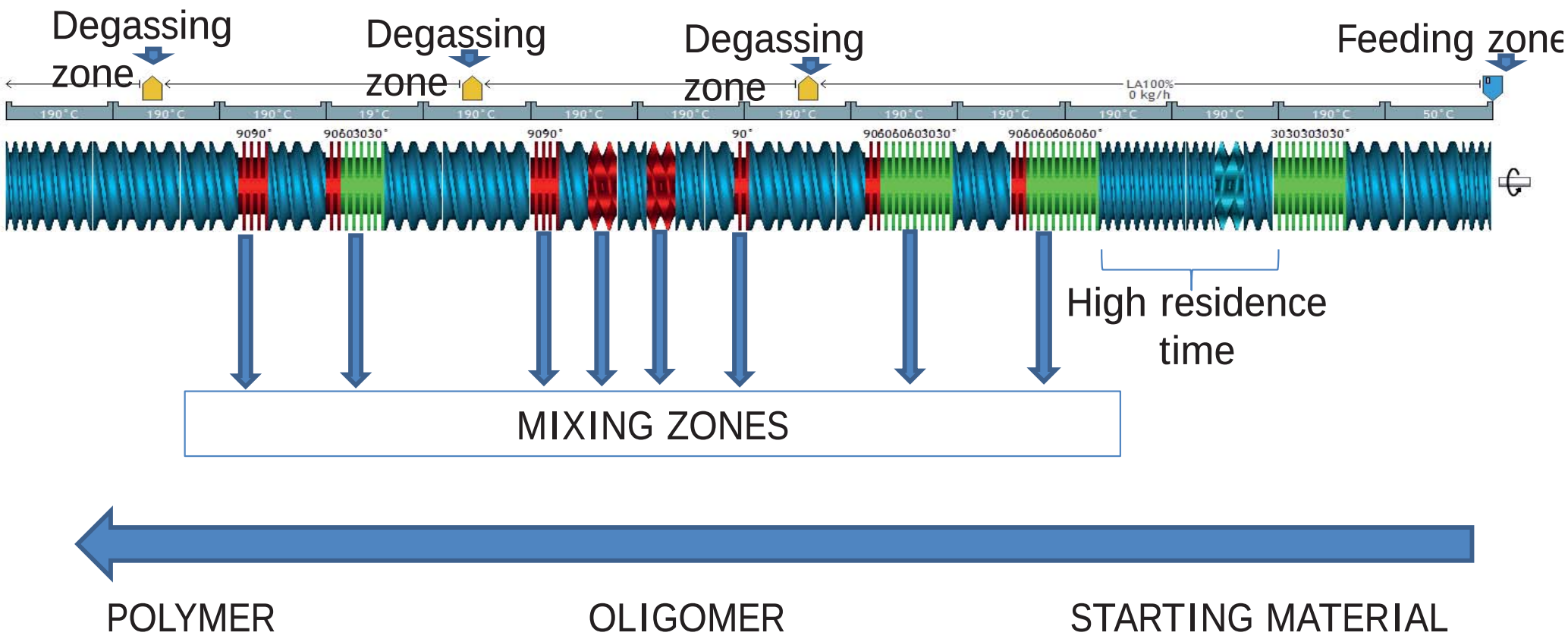
- The screw configuration and processing conditions are designed with **Ludovic software**.

- Select the initial processing conditions taking into account the **mean residence time (REX lab optimization)**

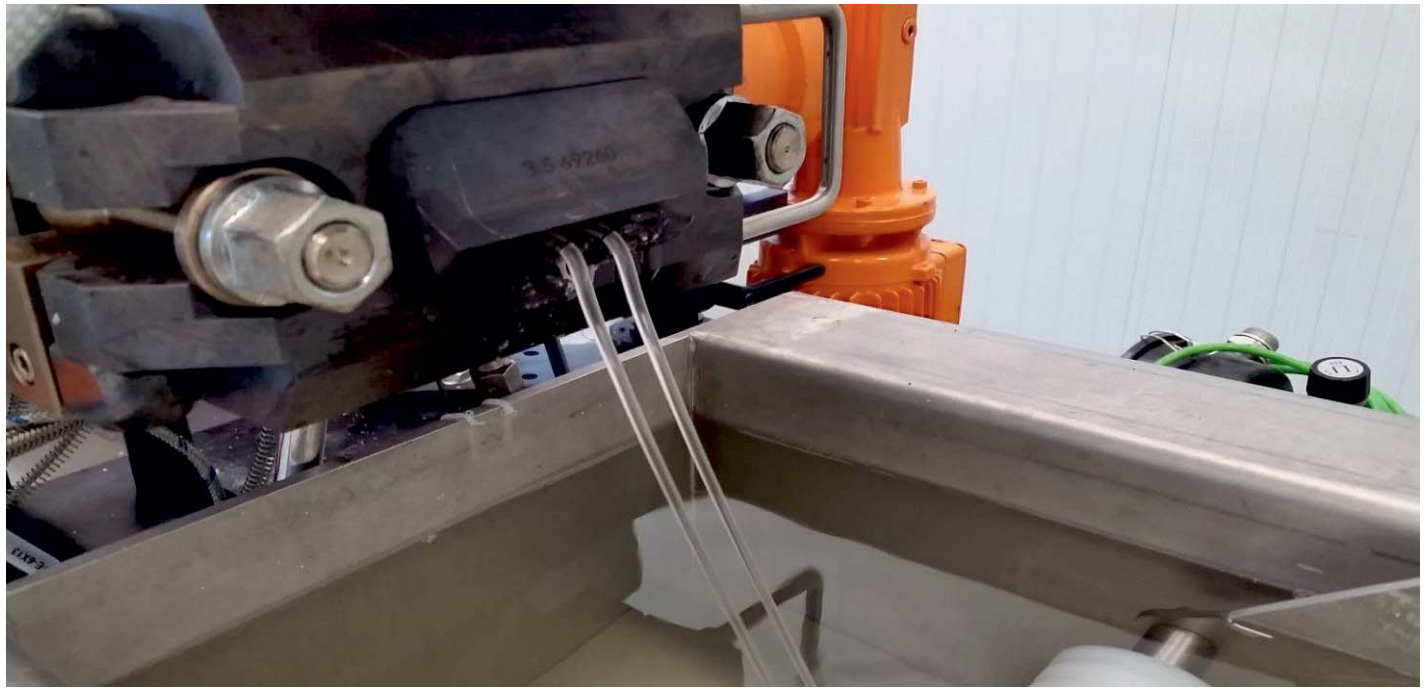
Polymerization methods: PLA-glutaric copolymers.



Polymerization methods: PLA-glutaric copolymers.



Polymerization methods: PLA-glutaric copolymers.

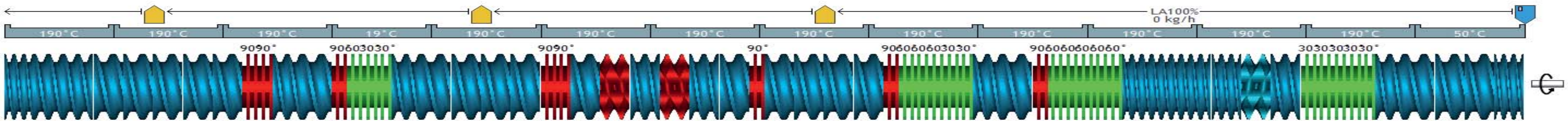


Production:
4 kg/h

LOW LACTIDE CONTENT
IN DEGASSING ZONES

Polymerization methods: PLA-glutaric copolymers.

Polymerization methods: PLA-glutaric copolymers.



SAMPLE	M22	M23
Temperature (ºC)	240-250	230-240
Speed rotation (rpm)	30	30
Throughout (kg/h)	4	4
Colour	honey	Transparent
Conversion (%)	>99	>99

It is observed an increase in the pressure during the REX (26 bar)

Temperature peak activate the reaction and increase the yield.

Polymerization methods: PLA-glutaric copolymers.

SAMPLE	M22	M23	Natureworks
Mw	182533	166660	100000-200000
Mn	130375	121271	
PDI	1,4	1,4	1,74
Mp (ºC)	174,3	169,9	165,9
Crystallinity (%)	7,0	6,6	45
Tg (ºC)	55,5	53,3	64,1

Polymerization methods: PLA-glutaric copolymers.

After annealing process 2h/75ºC

SAMPLE	M22	M23	Natureworks
Mp (ºC)	171,8	171,8	165,9
Crystallinity (%)	15,6	42,8	45
Tg (ºC)	54,5	54,3	64,1

Polymerization methods: PLA-glutaric copolymers.

- ✓ Polymerization of PLA and copolymers have been optimized
- ✓ Ecopoltech has optimized the synthesis of starting materials.
- ✓ AIMPLAS has optimized the REX process up to 4 kg/h in pilot plant extruders.
- ✓ Biopolyester derived from glutaric have been developed for packaging aplications

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Characterization

Characterization methods

- GPC analysis
- Acid number and Hydroxyl number by Anh acetic titration ASTM D4274
- DSC for thermal characterization
- Fast method for MW characterization in cooperation with University of Almeria.

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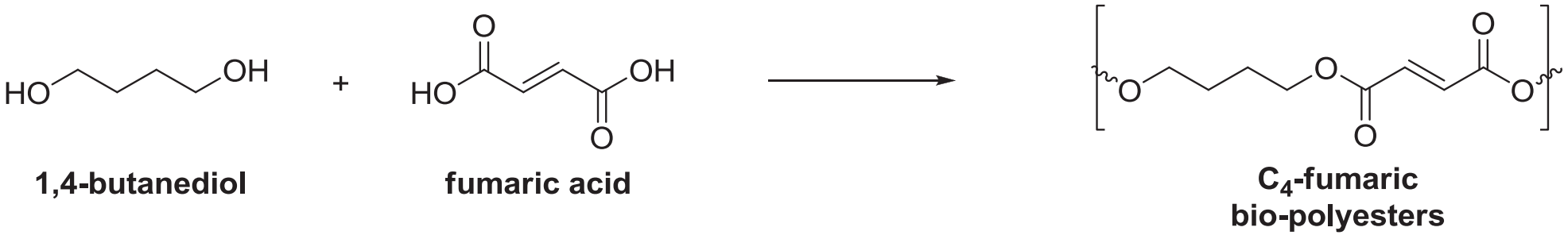
Characterization methods

MW determination by NMR tools



1,4-butanediol

fumaric acid

C_4-fumaric bio-polyesters

GPC *vs* NMR

Mw GPC-LS-RI	D (10^{-9})	Mw NMR	diff (%)
1320	0.4224	1397	5.81
5970	0.1997	5612	5.99
10100	0.1512	8986	11.03
60000	0.0537	59190	1.35
460000	0.0171	437746	4.84

Characterization methods

MW determination by NMR tools

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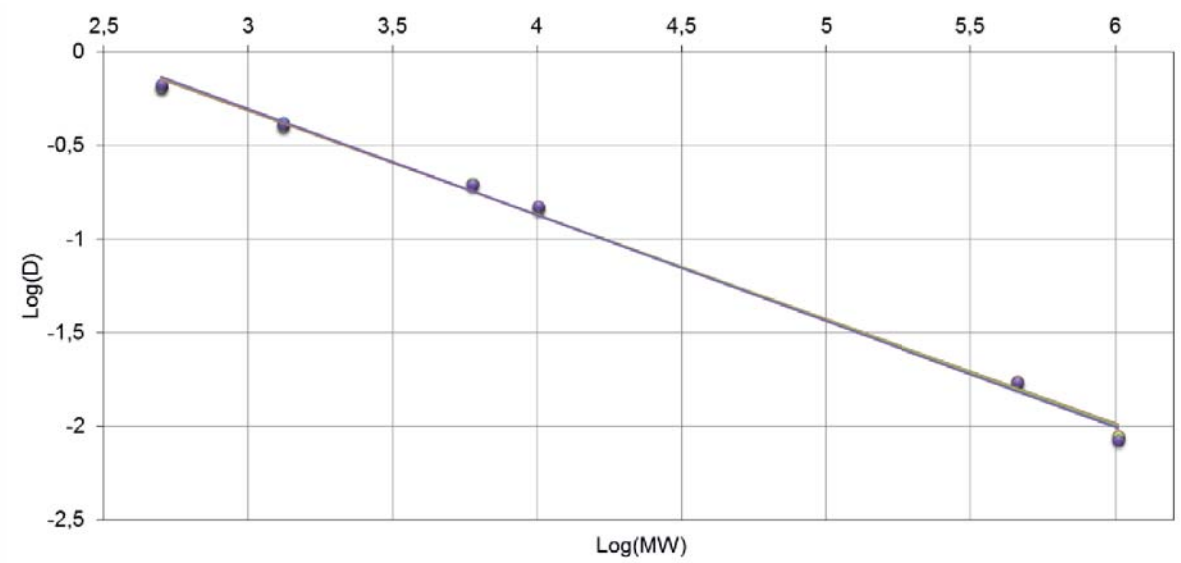
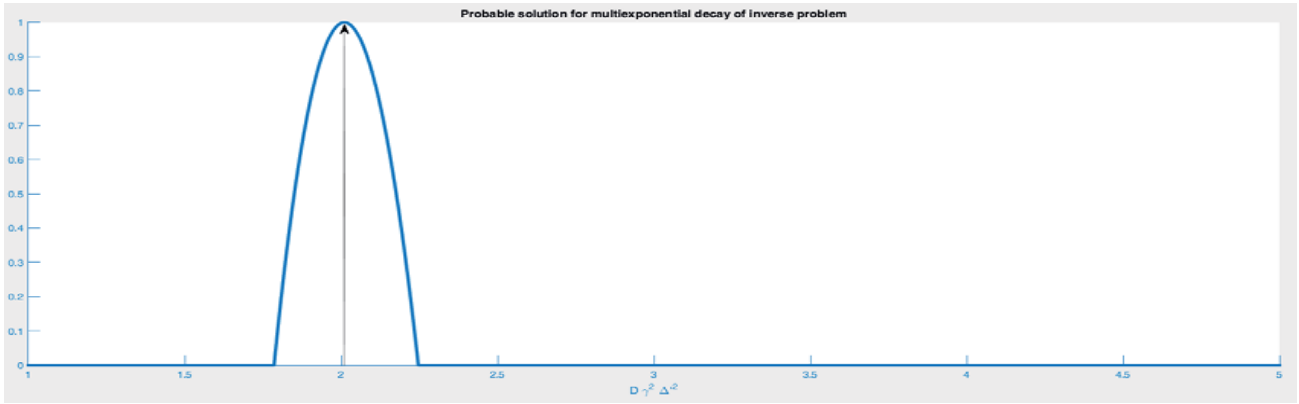
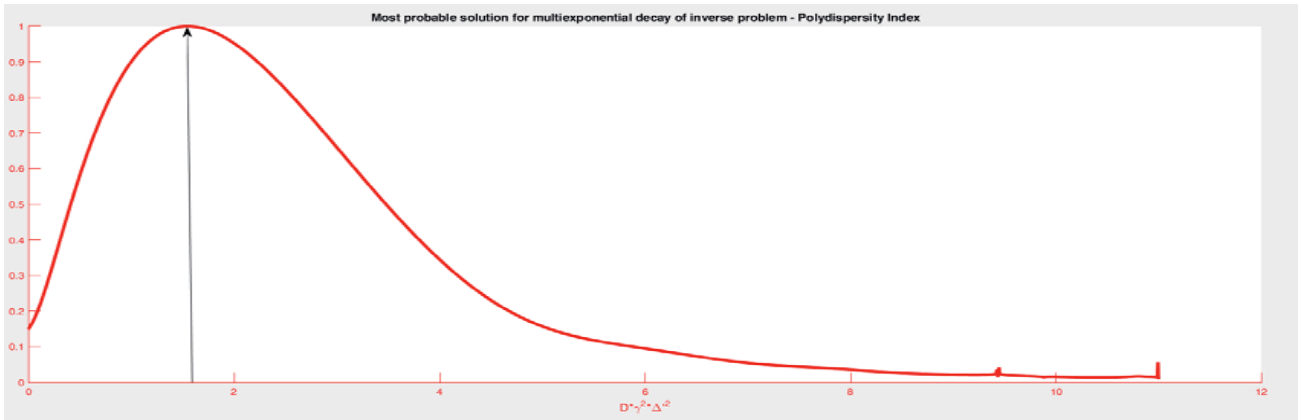
-Based on the linear correlation between the logarithm of diffusion coefficient (logD) and the molecular weights (log Mw).



Characterization methods

MW determination by NMR tools (PDI)





Mathematical models are available for Biorefine2G and other polymers

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BIOREFINE-2G

Summary

Summary:

- ✓ BIOTREND has optimized the biofumaric purification at “polymer grade”
- ✓ Biopolyester derived from biofumaric acid have been developed for biomedical aplications.
- ✓ Polymerization of PLA glutaric derivatives is available.
- ✓ Reactive extrusion process is ready for industrial production of PLA and PLA copolymers.
- ✓ Fast method for MW characterization is available.

Thank you for your attention !!

amgarcia@aimplas.es

www.aimplas.net

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INSTITUTO TECNOLÓGICO
DEL PLÁSTICO

bioREFINE-2G

Project No. FP7-613771

SEVENTH FRAMEWORK PROGRAMME