Summary of selected publications:

- ❑ **Development of sustainable polyester packaging Materials**

  (Next-generation Bioplastics based on 2,5-furandicarboxylic acid)

- ❑ **Chemical Recycling of post-consumer "polyester type" Plastics**

NEJIB KASMI

One page resume **Nejib KASMI** | Mail: nejibkasmi@gmail.com | Current address: Amsterdam, Netherlands |
PhD in Polymer Chemistry | Website: https://nejibkasmi.com/ | Tel: +31617357898 | (Detailed CV: here) |

- **Highly skilled Polymer Scientist, Development of sustainable Polyesters from renewable resources**
- Researcher with strong international network and work experience in several leading European research groups

Peer-reviewed articles: **27** (Complete publications list here) | h-Index: **18**, Citations: **865**

Top Co-authors: Prof. Dimitrios BIKIARIS (**21**) (LINK) Prof. George PAPAGEORGIOU (**20**) (LINK)

- Member of ACS Biomacromolecules Early Career Board (2024) Biomacromolecules LINK
- Scientific Societies: European network of FURAN based chemicals and materials FOR a Sustainable development (COST Action CA18220, LINK) ▪ Reviewer of Elsevier *Q1* journals (details)
- Guest Editor of Special Issue "**Development of High-Performance Biobased Polyesters**" in Polymers (Q1)

A solid scientific background and proven track-record in developing fully biobased polyesters — made from renewable monomers — for sustainable Packaging Materials

EXPERTISE /JOB-RELATED SKILLS: ▪ Development of sustainable polyester packaging Materials

▪ Bioplastics based on 2,5-furandicarboxylic acid ▪ Chemical recycling of plastics waste :

- In-depth knowledge and technical understanding of the Design, Synthesis, and Study of fully biobased polymers, mainly homopolyesters, copolyesters, polyester blends and functionalized branched polyesters derived from 2,5-furandicarboxylic acid (FDCA) and other renewable monomers (isosorbide, vanillic acid,...).
- Chemical recycling of post-consumer '*polyester-type*' plastics to value added circular materials by utilizing dynamic covalent chemistry/Integrating plastic waste in the circular economy/plastic waste management.
- Excellent command of several synthesis techniques of Polyesters: Melt Polycondensation, Solid state Polycondensation, Polymer Blending, Ring-Opening Polymerization, In Situ polymerization, etc.
- Furan-based Bioplastics: Sustainable polyesters, copolyesters, polyester Blends, Isocyanate-free polyester-urethane networks derived from FDCA / Investigation of crystallization, melting behavior, mechanical performance, and "enzymatic / in soil" biodegradability of renewable (Co-)polyesters / biobased branched polyesters and polyester-urethanes / Organic chemistry / (Microwave-assisted) organic synthesis
- **Teaching experience** of Master's students (104 h) at KTH Royal Institute of Technology in Stockholm.
- Effective supervision skills (acquired through my experience as co-supervisor of MSc and PhD students).

PRESENTATIONS AT INTERNATIONAL CONFERENCES (Details here)

- **15** communications at **14** international conferences (in Sweden, France, Italy, Greece, Belgium, Portugal)

AWARDS (Details here) :

- July 13, 2018 **Best Presentation Award** at the IUPAC Postgraduate Summer School on Green Chemistry - Venice, Italy, awarded by L'ORÉAL PARIS and **Eni** Groups.

PROFESSIONAL & WORK EXPERIENCE

- 12/2023 –present **R&D project Leader / Polymer Scientist**
  Avantium company (LINK) - Amsterdam, Netherlands
- 04/2023 – 11/2023 **Researcher**
  Institute Charles Gerhardt Montpellier (CNRS) - Montpellier, France
- 11/2021 – 11/2022 **Researcher**
  KTH Royal Institute of Technology, Stockholm Sweden
  Research projects: - *Microwave-assisted chemical recycling of post-consumer "polyester type" plastics* (Research output: LINK)
  - *Highly transparent biobased polyurethane thermosets with "on demand" tunable properties and enzymatic degradability* (LINK).
  - **In 2022**: Teaching "**Polymer Physics course**" (KF2140) to first-year Master students (104 hours) at **KTH**
- 06/2021 – 10/2021 **Research Scientist**
  Helmholtz-Zentrum Hereon, Berlin - Germany
  Research project: *Synthesis of multifunctional polyester-based biomaterials for adaptive and active polymer systems*
- 03/2019 – 04/2021 **Jr. Research & Technology Associate**
  Luxembourg Institute of Science and Technology, Luxembourg
  Research project: *New biopolymers based on renewable building blocks from catalytic deoxygenation of hemicellulose*
- 04/2018 – 10/2018 **Postdoctoral Fellowship**
  BIKIARIS Group - Aristotle University of Thessaloniki, Greece
  Research project: *Furan-based Polyesters*
- 07/2017 – 03/2018 Temporary Research Fellowship
  BIKIARIS Group - Aristotle University of Thessaloniki, Greece
- 09/2016 – 06/2017 Mobility **Erasmus+** grant
  BIKIARIS Group - Aristotle University of Thessaloniki, Greece
- 04/2016–07/2016 **Research Assistant** - Padova University, Italy
- 05/2014 – 04/2016 3 PhD Internships
  Universities of Padova and Bologna, Italy

EDUCATIONAL QUALIFICATIONS Monastir University, Tunisia

- 03/2018 **PhD in Polymer chemistry** (Merit: Very honorable)
  PhD dissertation: **Valorisation of Isosorbide: Synthesis of new functional polymers**
- 11/2013 **Master's Degree in Organic Chemistry**
- 06/2011 **Bachelor's degree in chemistry**

Effective supervision skills

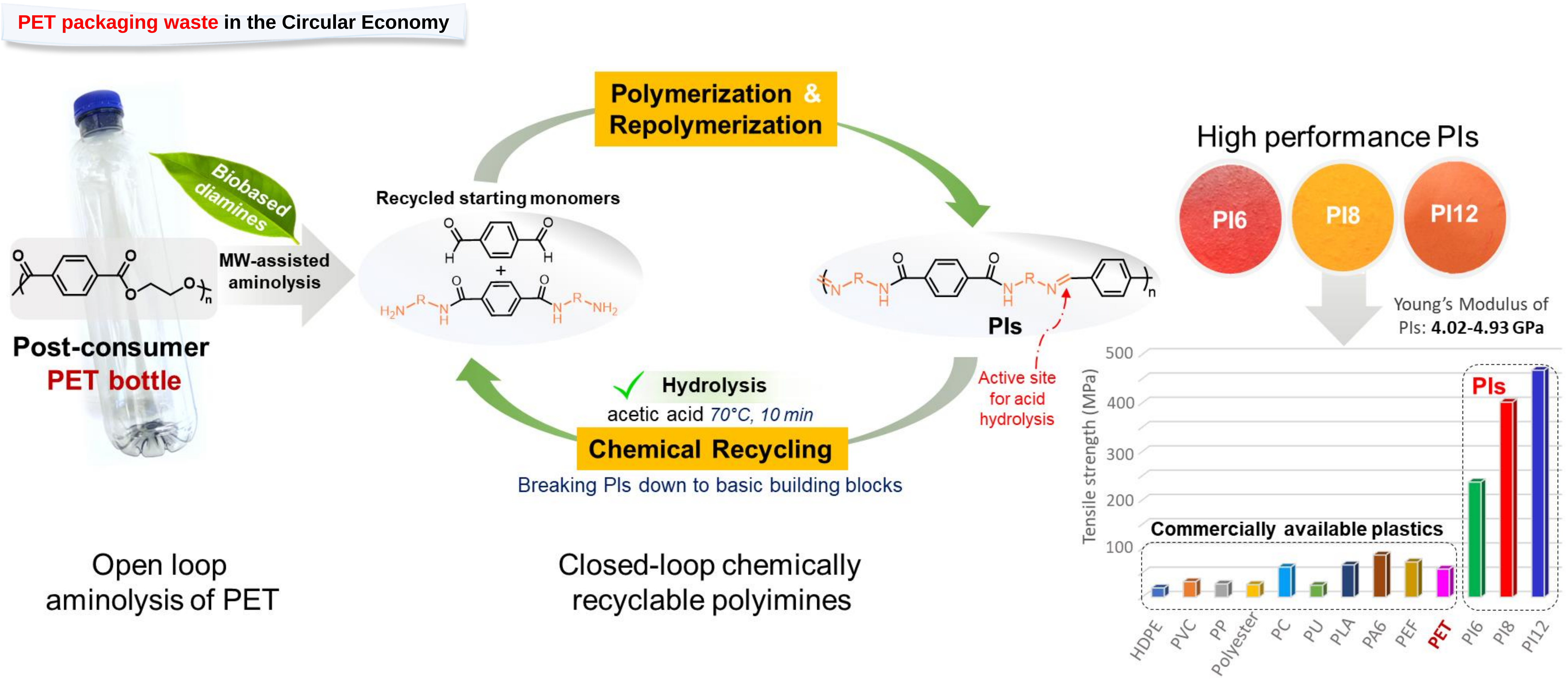
➢ *acquired through my experience as co-supervisor of BSc, MSc and PhD students:*

Name and University of supervisee	Research outputs (Publications)
Yosra Chebbi, *PhD student* *Aristotle University of Thessaloniki, Greece*	▪ N. Kasmi*, Z. Terzopoulou, *Y. Chebbi,* R. Dieden, Y. Habibi, D.N. Bikiaris, *Polymer Degradation and Stability* **2022**, 195, 109804. LINK ▪ *Y. Chebbi*, N. Kasmi, M. Majdoub, P. Cerruti, G. Scarinzi, M. Malinconico, G. Dal Poggetto, G.Z. Papageorgiou, D.N. Bikiaris*, *ACS Sustainable Chemistry and Engineering* **2019**, 7, 5501-5514. LINK ▪ *Y. Chebbi*, N. Kasmi, M. Majdoub, G.Z. Papageorgiou*, D.N. Achilias, D.N. Bikiaris*, *Polymers* **2019**, 11, 438. LINK ▪ N. Kasmi, L. Papadopoulos, *Y. Chebbi*, G.Z. Papageorgiou, D.N. Bikiaris*, *Polymer Degradation and Stability* **2020**, 181, 109315. LINK
Carla PISANI, *Master student* *Luxembourg Institute of Science and Technology (LIST), Luxembourg*	▪ M. Safari, N. Kasmi, *C. Pisani*, V. Berthé, A. J. Müller*, Y. Habibi, *International Journal of Biological Macromolecules* **2022**, 214, 128-139. LINK
Mohamed Wahbi, *Master student* *Aristotle University of Thessaloniki, Greece*	▪ N. Kasmi, *M. Wahbi*, L. Papadopoulos, Z. Terzopoulou, N. Guigo, N. Sbirrazzuoli, G.Z. Papageorgiou*. D.N. Bikiaris*, *Polymer Degradation and Stability.* **2019**, 160, 242- 263. LINK ▪ Z. Terzopoulou, *M. Wahbi*, N. Kasmi, G.Z. Papageorgiou, D.N. Bikiaris*, *Thermochimica Acta* **2020**, 686, 178549. LINK ▪ L. Papadopoulos, A. Zamboulis, N. Kasmi, *M. Wahbi*, C. Nannou, D. A. Lambropoulou, M. Kostoglou, G. Z. Papageorgiou, D. N. Bikiaris*, *Green Chemistry* **2021**, 23, 2507-2524. LINK
Elena Agapiou, *Master student* *Aristotle University of Thessaloniki, Greece*	▪ N. Kasmi, N. Ainali, *E. Agapiou*, L. Papadopoulos, G.Z. Papageorgiou. D.N. Bikiaris*, *Polymer Degradation and Stability* **2019**, 169, 108983. LINK
Nina Maria Ainali, *Master student* *Aristotle University of Thessaloniki, Greece*	▪ N. Kasmi, *N. Ainali*, E. Agapiou, L. Papadopoulos, G.Z. Papageorgiou. D.N. Bikiaris*, *Polymer Degradation and Stability* **2019**, 169, 108983. LINK

➢ *through my teaching experience at KTH, Stockholm in 2022:* "Polymer Physics course" (KF2140) to 1st-year master students (104 hours)

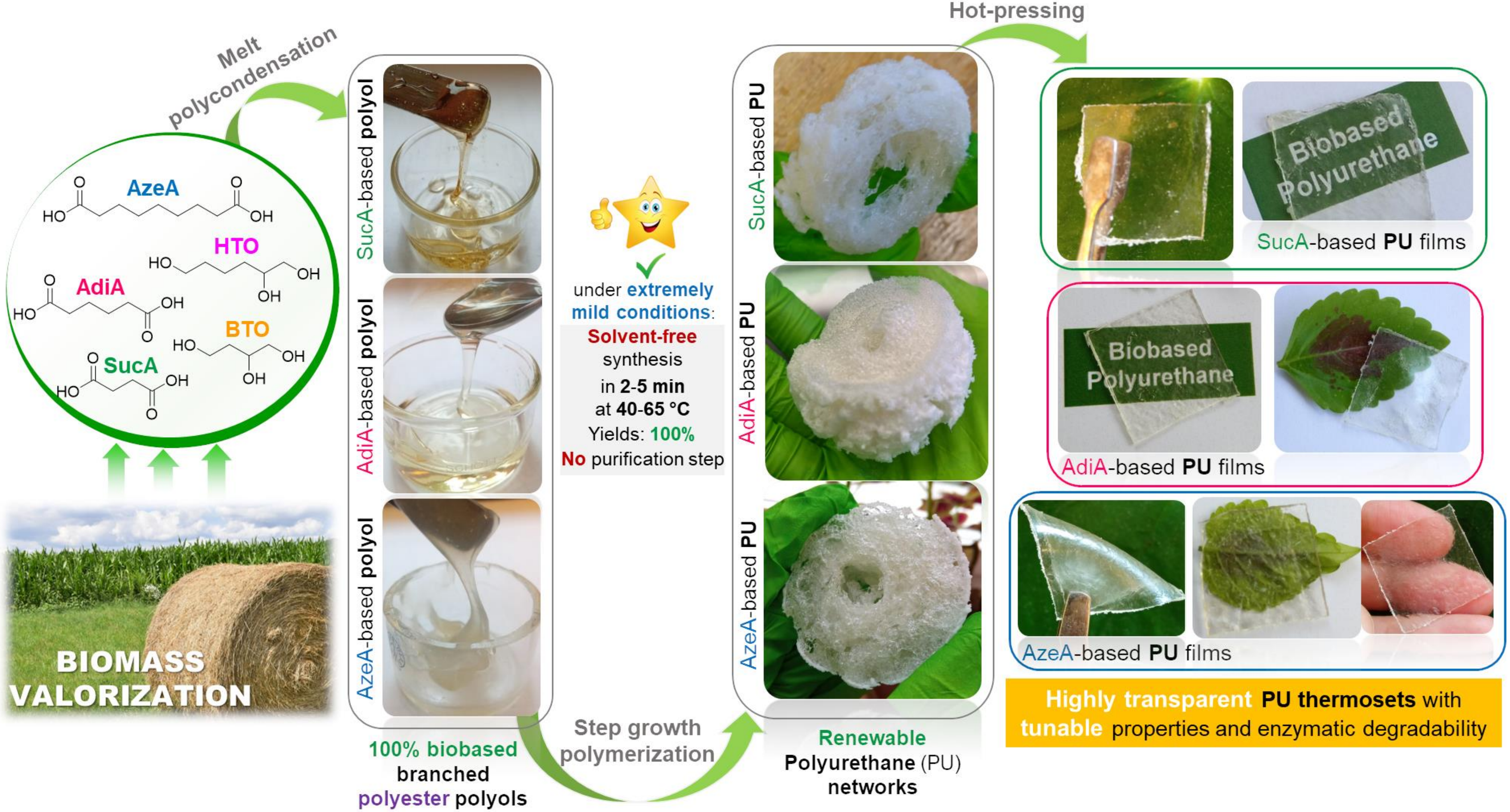
Work done at KTH

1. Open-loop recycling of post-consumer PET to closed-loop chemically recyclable high-performance polyimines

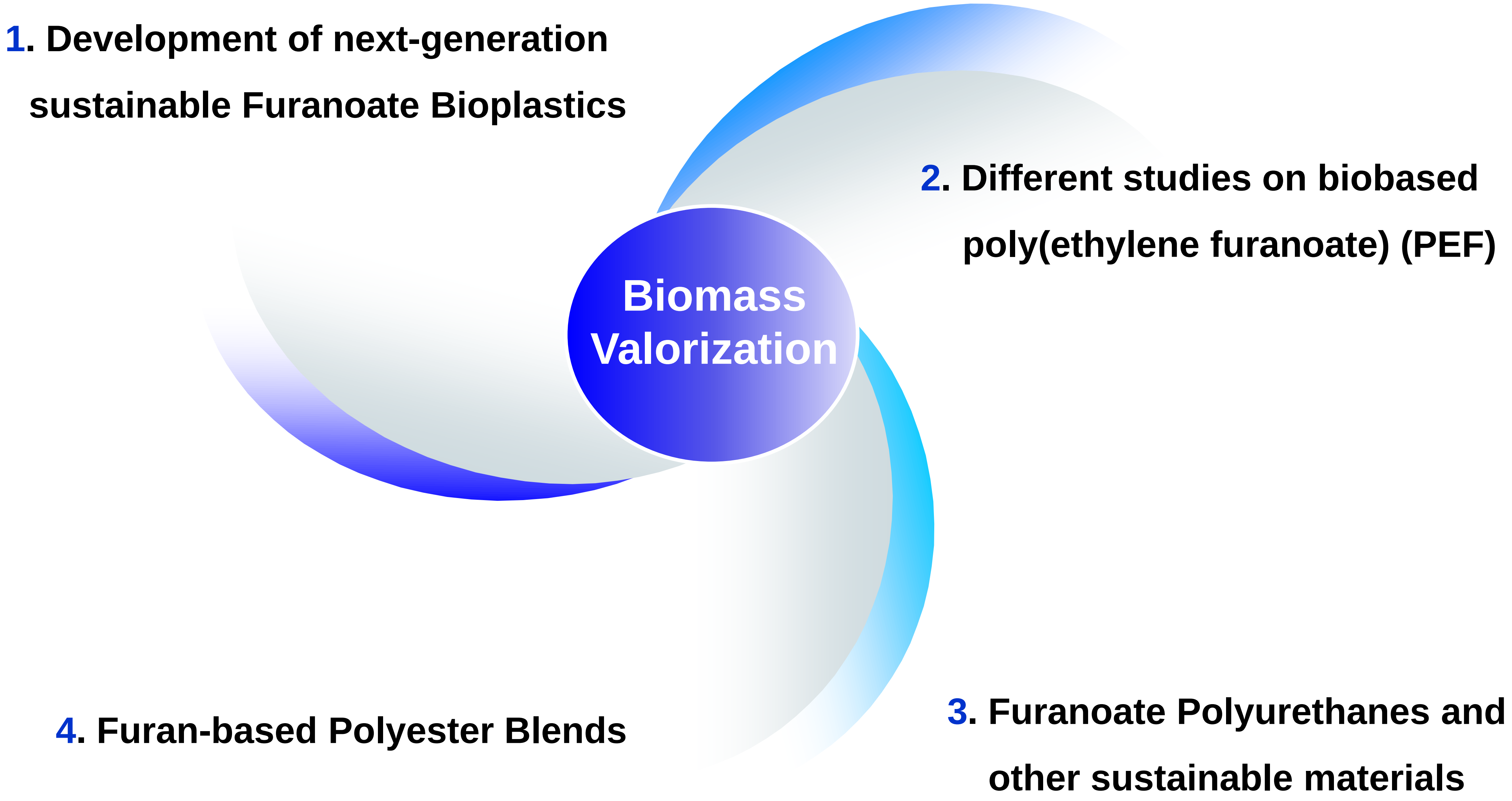


N. Kasmi, E. Bäckström, M. Hakkarainen*. Open-loop recycling of post-consumer PET to closed-loop chemically recyclable high-performance polyimines, *Resources, Conservation and Recycling journal (Q1)* **2023**, *193*, 106974 (LINK) *(Due to the quality of the work, this paper was selected by the Editor as the **Cover article** of the volume 193, June 2023!)*

2. Highly transparent polyurethane thermosets with tunable properties and enzymatic degradability derived from polyols originating from hemicellulosic sugars



N. Kasmi*, Y. Chebbi, A. Lorenzetti, M. Hakkarainen*. Highly transparent polyurethane thermosets with tunable properties and enzymatic degradability derived from polyols originating from hemicellulosic sugars, *Green Chemistry (Q1)* **2023**, *25*, 9908-9925 (LINK)


1. Development of next-generation
sustainable Furanoate Bioplastics
Biomass
Valorization
2. Different studies on biobased
poly(ethylene furanoate) (PEF)
3. Furanoate Polyurethanes and
other sustainable materials
4. Furan-based Polyester Blends

1. Development of next-generation sustainable Furanoate Bioplastics

Copolyesters derived from 2,5-furandicarboxylic acid

RETURN TO ISSUE | < PREV | **RESEARCH ARTICLE** | NEXT >

LINK

Synthesis, Characterization, and Biodegradability of Novel Fully Biobased Poly(decamethylene-*co*-isosorbide 2,5-furandicarboxylate) Copolyesters with Enhanced Mechanical Properties

Yosra Chebbi, Nejib Kasmi, Mustapha Majdoub, Pierfrancesco Cerruti, Gennaro Scarinzi, Mario Malinconico, Giovanni Dal Poggetto, George Z. Papageorgiou , and Dimitrios N. Bikiaris*

Cite this: *ACS Sustainable Chem. Eng.* 2019, 7, 5, 5501–5514
Publication Date: February 12, 2019
https://doi.org/10.1021/acssuschemeng.8b06796
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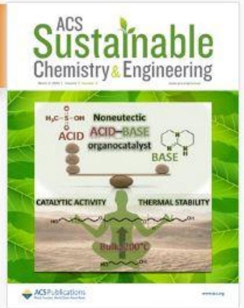


ACS Sustainable Chemistry & Engineering

Polymer Degradation and Stability
Volume 195, January 2022, 109804

LINK

Tuning thermal properties and biodegradability of poly(isosorbide azelate) by compositional control through copolymerization with 2,5-furandicarboxylic acid

Nejib Kasmi [a] [1], Zoi Terzopoulou [b], Yosra Chebbi [b], Reiner Dieden [a], Youssef Habibi [a], Dimitrios N. Bikiaris [b]

Polymer Degradation and Stability
Volume 152, June 2018, Pages 177-190

Synthesis and crystallization of new fully renewable resources-based copolyesters: Poly(1,4-cyclohexanedimethanol-co-isosorbide 2,5-furandicarboxylate)

LINK

Nejib Kasmi [a, b], Mustapha Majdoub [b], George Z. Papageorgiou [c], Dimitrios N. Bikiaris [a]

Polymer Degradation and Stability
Volume 169, November 2019, 108983

LINK

Novel high T_g fully biobased poly(hexamethylene-co-isosorbide-2,5-furan dicarboxylate) copolyesters: Synergistic effect of isosorbide insertion on thermal performance enhancement

Nejib Kasmi [a], Nina Maria Ainali [a], Elena Agapiou [a], Lazaros Papadopoulos [a], George Z. Papageorgiou [b], Dimitrios N. Bikiaris [a]

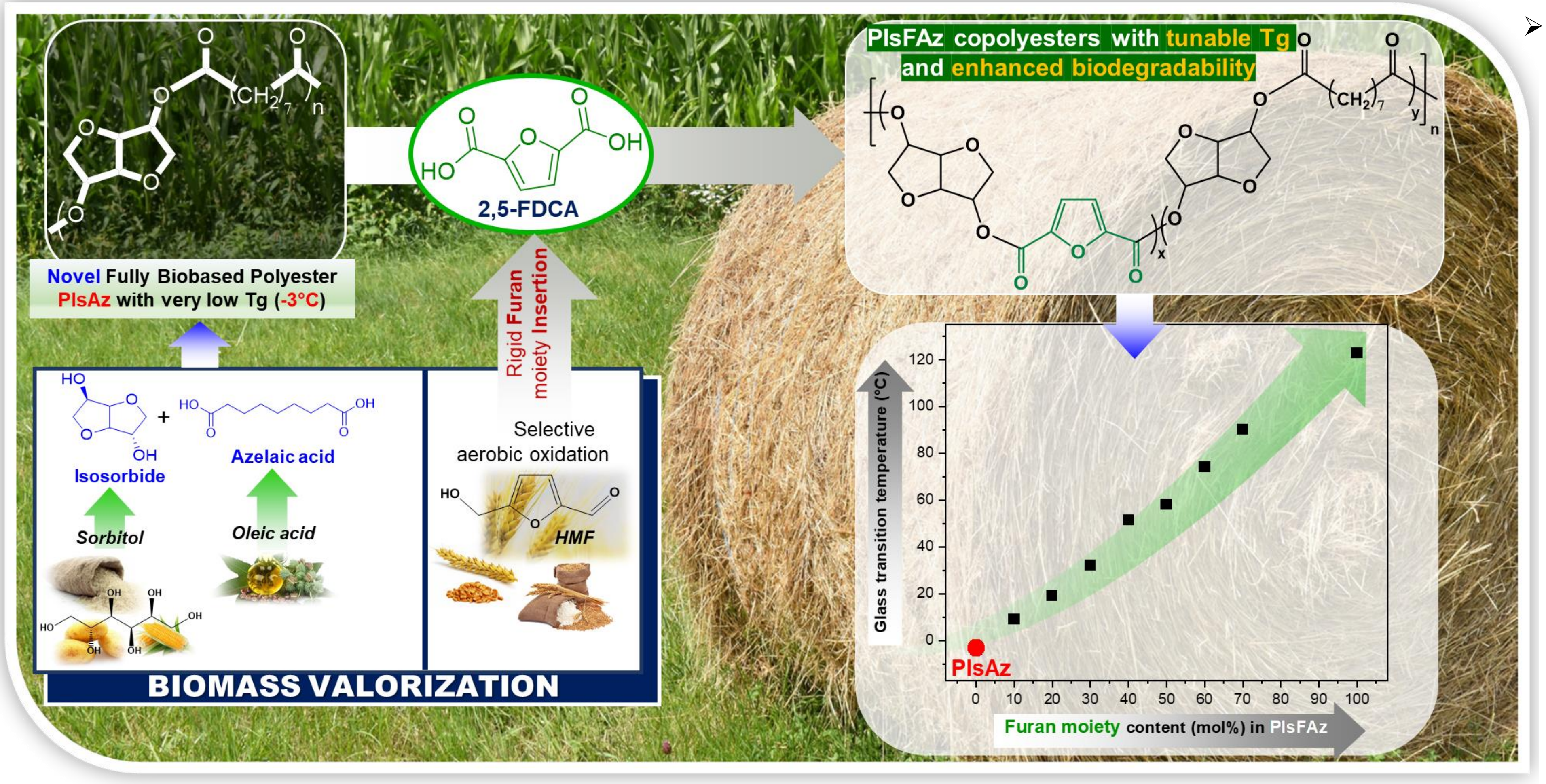
Polymer Degradation and Stability
Volume 160, February 2019, Pages 242-263

Synthesis and characterization of two new biobased poly(pentylene 2,5-furandicarboxylate-co-caprolactone) and poly(hexamethylene 2,5-furandicarboxylate-co-caprolactone) copolyesters with enhanced enzymatic hydrolysis properties

Nejib Kasmi [a], Mohamed Wahbi [a], Lazaros Papadopoulos [a], Zoi Terzopoulou [a], Nathanaël Guigo [b], Nicolas Sbirrazzuoli [b], George Z. Papageorgiou [c], Dimitrios N. Bikiaris [a]

LINK

A very efficient route for enhancing the T_g of copolymers through controlled incorporation of FDCA moiety into polyester backbone



- **Enhanced susceptibility to enzymatic hydrolysis** with a maximum degradation rate up to **61%** after 30 days.
- **Improved thermal performance**:

-tunable T_g over a high and broad temperature window oscillating from 9 to 91 °C

-good resistance to heat as totally amorphous materials

-very wide temperature window of safe heat processing above their T_g

Novel class of high-performance furanoate bioplastics to be a promising alternative to replace their petroleum-derived analogues

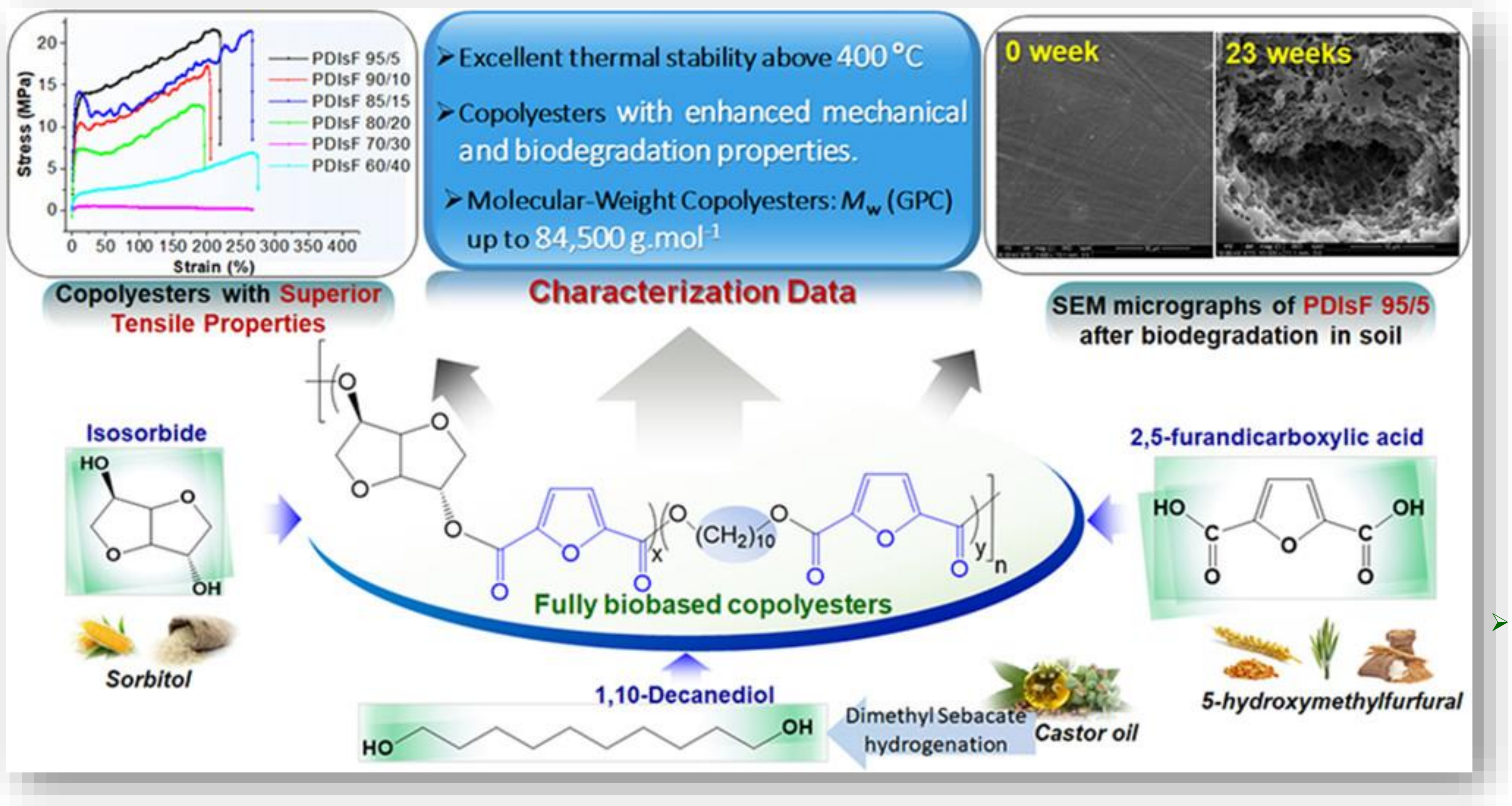
N. Kasmi,* Z. Terzopoulou, Y. Chebbi, R. Dieden, Y. Habibi, D.N. Bikiaris. Tuning thermal properties and biodegradability of isosorbide-based polyester by compositional control through copolymerization with 2,5-furandicarboxylic acid, *Polymer Degradation and Stability (Q1)* **2022**, *195*, 109804 (LINK)

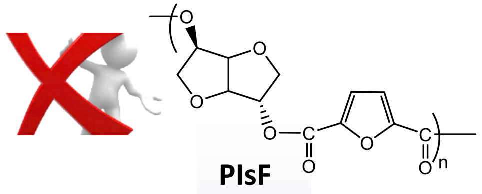
Development of next-generation Furanoate Bioplastics

Different studies on biobased poly(ethylene furanoate) (PEF)

Furanoate Polyurethanes and other sustainable materials

Furan-based Polyester Blends





Total absence of crystallinity

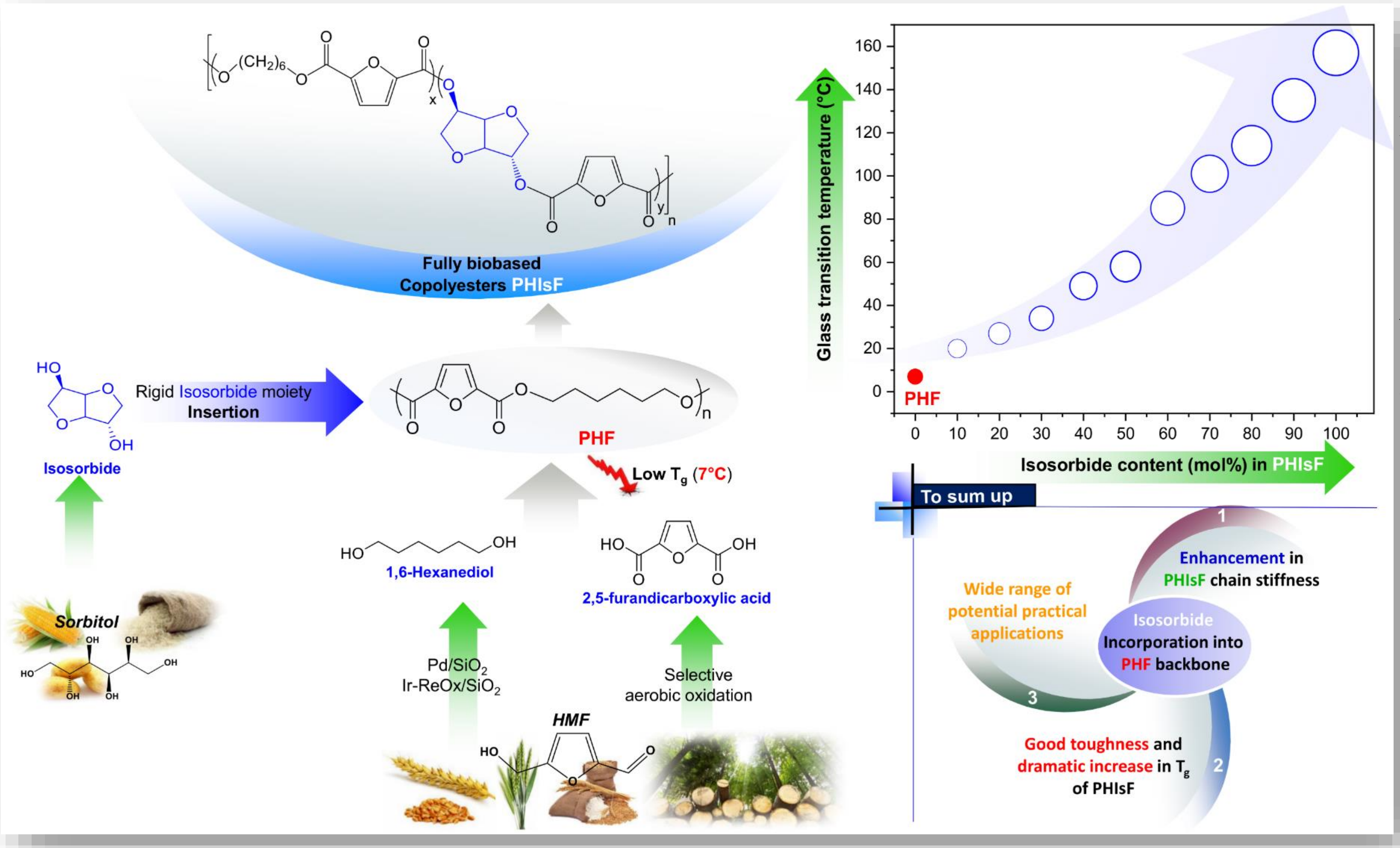
Copolymerization with **highly crystalline** long-chain aliphatic polyester

poly(decamethylene 2,5-furandicarboxylate)

➢ **Developing next-generation sustainable bioplastics from renewable raw materials**

Y. Chebbi, **N. Kasmi**, M. Majdoub, P. Cerruti, G. Scarinzi, M. Malinconico, G. Dal Poggetto, G.Z. Papageorgiou, D.N. Bikiaris*. Synthesis, Characterization, and Biodegradability of Novel Fully Biobased Poly(decamethylene-co-isosorbide 2,5-furandicarboxylate) Copolyesters with Enhanced Mechanical Properties, *ACS Sustain. Chem. Eng. (Q1)* **2019**, *7*, 5501-5514 (LINK)

Effective solution for overcoming the low T_g of the fully biobased poly(hexamethylene 2,5-furan dicarboxylate) (PHF)



- Synthesis of highly heat-resistive poly(hexamethylene-co-isosorbide-2,5-furandicarboxylates) copolyesters

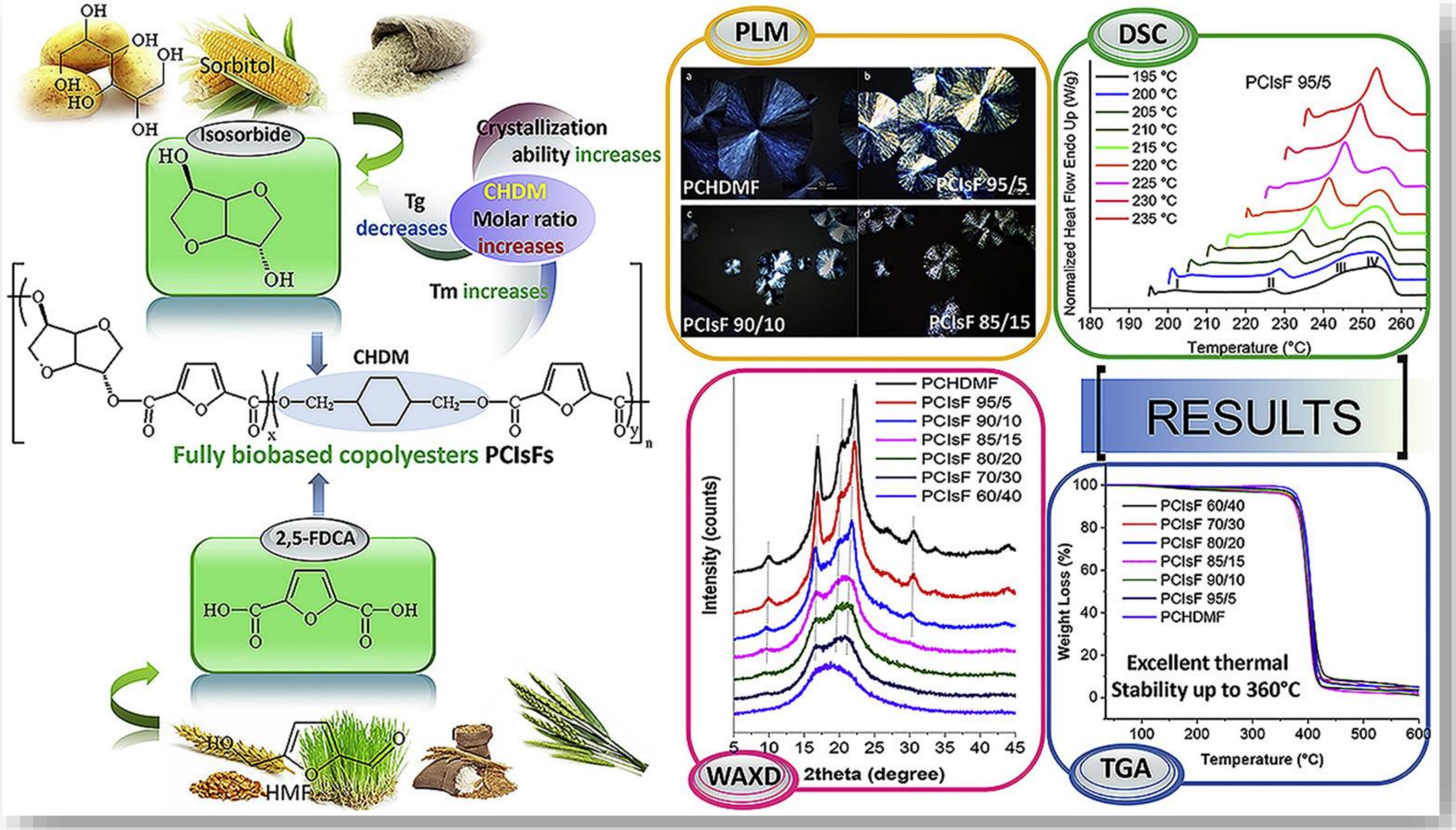
✓ Great resistance to heat up to 360 °C (**$T_{d,5\%}$**)

✓ Very wide T_g range: 10 °C < **T_g** < 135 °C

✓ Wholly amorphous materials (except for extremely low contents in Isosorbide)

PHIsF have the potential to serve as promising fully biobased amorphous materials for practical applications **that demand high T_g values**.

N. Kasmi, N. Ainali, E. Agapiou, L. Papadopoulos, G.Z. Papageorgiou. D.N. Bikiaris*. Novel High Tg fully biobased poly(hexamethylene-co-isosorbide-2,5-furan dicarboxylate) Copolyesters: Synergistic Effect of Isosorbide Insertion on Thermal performance Enhancement, *Polym. Degrad. Stab. (Q1)* **2019**, *169*, 108983 (LINK)



➢ **Fully biobased poly(1,4-cyclohexanedimethanol-co-isosorbide 2,5-furandicarboxylate)s (PCIsFs):**

- ✓ Controlled crystallization rates
- ✓ enhanced thermal-properties were achieved by isosorbide insertion.
- ✓ Excellent thermal stability up to 360 °C
- ✓ An obvious **structure-thermal properties relationship** in PCIsFs was found:

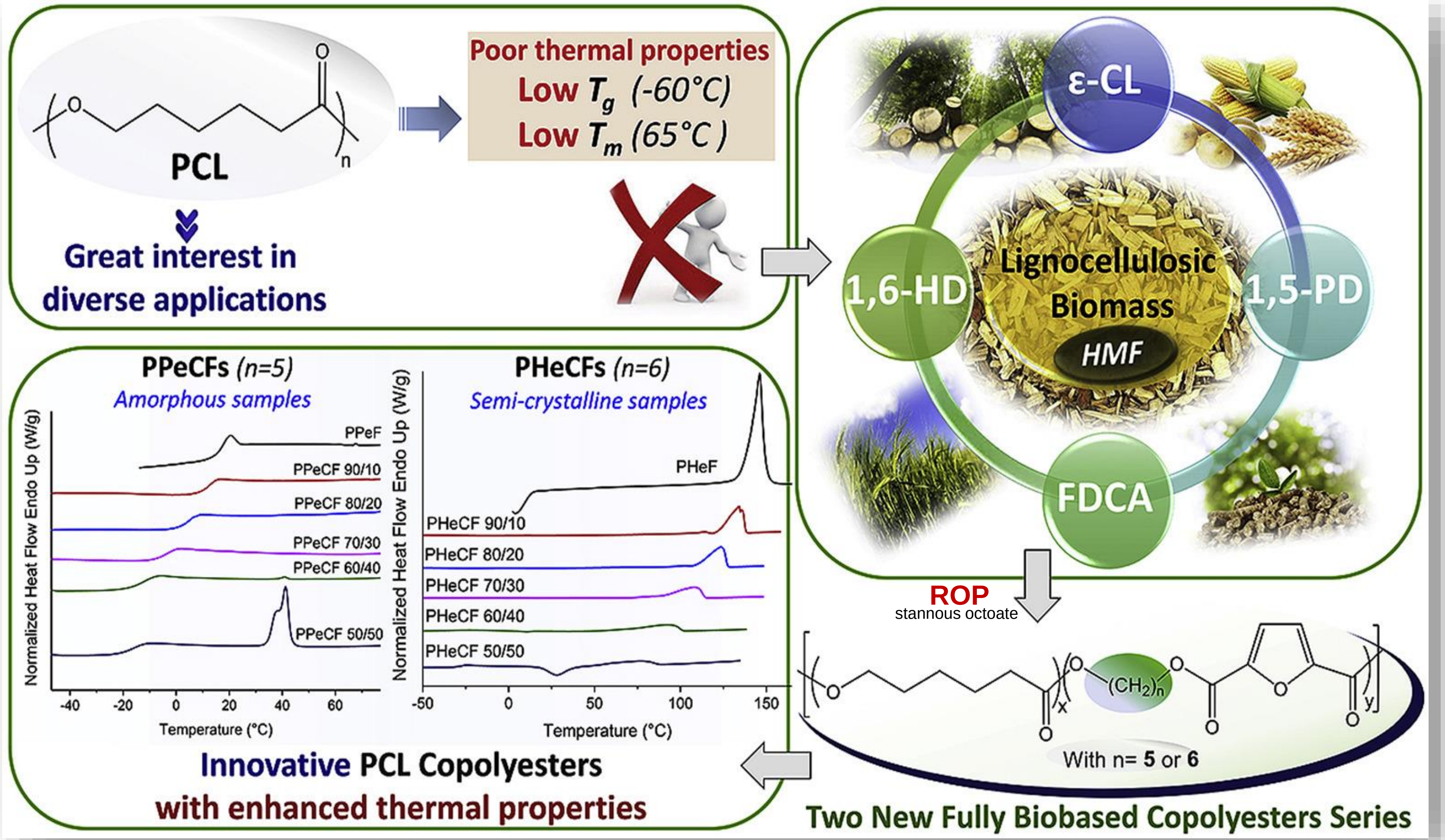
Isosorbide molar ratio ↗ → $\mathbf{T_g}$ ↗ and $\mathbf{T_c}$, $\mathbf{T_m}$ ↘

219.7°C < $\mathbf{T_m}$ < 257.2°C

161°C < $\mathbf{T_c}$ < 204°C

76.8°C < $\mathbf{T_g}$ < 103.5°C

N. Kasmi, M. Majdoub, G.Z. Papageorgiou*, D.N. Bikiaris*. Synthesis and crystallization of new fully renewable resources-based copolyesters: Poly(1,4-cyclohexanedimethanol-co-isosorbide 2,5-furandicarboxylate), *Polym. Degrad. Stab. (Q1)* **2018**, *152*, 177-190 (LINK)



- Thermal Degradation mechanism study (Pyrolysis-GC/MS):

  Identification of pyrolysis products of both copolyesters series

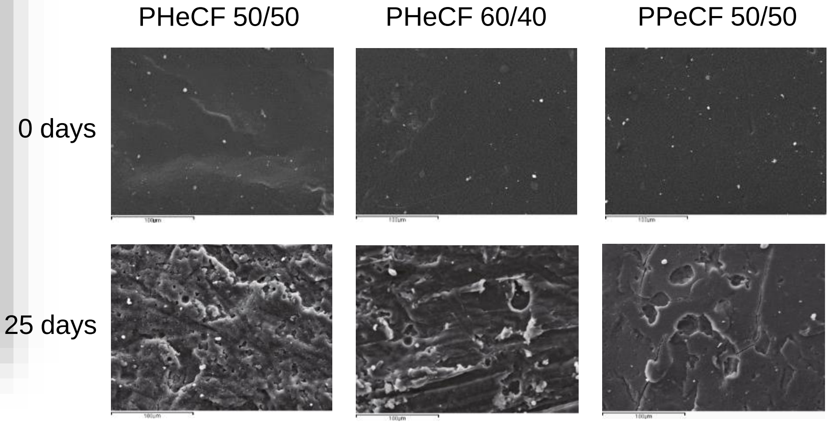
- Blocky microstructures with enhanced thermal properties:

  (*above those of neat **PCL***)

• PPeCFs	• PHeCFs
-16°C < T_g < 17°C	-28°C < T_g < 0°C
$T_{d,5\%}$ up to 365 °C	76°C < T_m < 146°C
	$T_{d,5\%}$ up to 310 °C

- Copolymers have high sensitivity to enzymatic hydrolysis:

  (*P. cepacia lipase* and *R. oryzae lipase*)



N. Kasmi, M. Wahbi, L. Papadopoulos, Z. Terzopoulou, N. Guigo, N. Sbirrazzuoli, G.Z. Papageorgiou*. D.N. Bikiaris*. Synthesis and characterization of two new biobased poly(pentylene 2,5-furandicarboxylate-co-caprolactone) and poly(hexamethylene 2,5-furandicarboxylate-co-caprolactone) copolyesters with enhanced enzymatic hydrolysis properties, *Polym. Degrad. Stab. (Q1)* **2019**, *160*, 242- 263 (LINK)

2. Different studies on biobased poly(ethylene furanoate) (PEF)

Solid-State Polymerization of Poly(ethylene furanoate) Biobased Polyester, I: Effect of Catalyst Type on Molecular Weight Increase

by Nejib Kasmi [1,2], Mustapha Majdoub [2], George Z. Papageorgiou [3,*], Dimitris S. Achilias [1] and Dimitrios N. Bikiaris [1,*]

1 Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
2 Laboratoire des Interfaces et Matériaux Avancés, Université de Monastir, 5000 Monastir, Tunisia
3 Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
* Authors to whom correspondence should be addressed.

LINK

Polymers **2017**, *9*(11), 607; https://doi.org/10.3390/polym9110607

ELSEVIER
Journal of Analytical and Applied Pyrolysis
Volume 126, July 2017, Pages 357-370

Effect of catalyst type on recyclability and decomposition mechanism of poly(ethylene furanoate) biobased polyester

LINK

Zoe Terzopoulou [a], Elisavet Karakatsianopoulou [a], Nejib Kasmi [b], Mustapha Majdoub [b], George Z. Papageorgiou [c], Dimitrios N. Bikiaris [a]

From the journal:
Green Chemistry

LINK

Investigation of the catalytic activity and reaction kinetic modeling of two antimony catalysts in the synthesis of poly(ethylene furanoate)†

Check for updates

Lazaros Papadopoulos, [a] Alexandra Zamboulis, [a] Nejib Kasmi, [a] Mohamed Wahbi, [a] Christina Nannou, [b] Dimitra A. Lambropoulou, [b] Margaritis Kostoglou, [c] George Z. Papageorgiou [d] and Dimitrios N. Bikiaris *[a]

Open Access Article

Solid-State Polymerization of Poly(Ethylene Furanoate) Biobased Polyester, II: An Efficient and Facile Method to Synthesize High Molecular Weight Polyester Appropriate for Food Packaging Applications

by Nejib Kasmi [1], George Z. Papageorgiou [2,*], Dimitris S. Achilias [1] and Dimitrios N. Bikiaris [1,*]

1 Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece
2 Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
* Authors to whom correspondence should be addressed.

LINK

Polymers **2018**, *10*(5), 471; https://doi.org/10.3390/polym10050471

Open Access Editor's Choice Article

Solid-State Polymerization of Poly(Ethylene Furanoate) Biobased Polyester, III: Extended Study on Effect of Catalyst Type on Molecular Weight Increase

by Yosra Chebbi [1,2], Nejib Kasmi [2], Mustapha Majdoub [1], George Z. Papageorgiou [3,*], Dimitris S. Achilias [2] and Dimitrios N. Bikiaris [2,*]

1 Laboratoire des Interfaces et Matériaux Avancés, Université de Monastir, Monastir 5000, Tunisia
2 Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece
3 Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
* Authors to whom correspondence should be addressed.

LINK

Polymers **2019**, *11*(3), 438; https://doi.org/10.3390/polym11030438

ELSEVIER
Thermochimica Acta
Volume 686, April 2020, 178549

LINK

Effect of additives on the thermal and thermo-oxidative stability of poly(ethylene furanoate) biobased polyester

Zoi Terzopoulou [a], Mohamed Wahbi [a], Nejib Kasmi [a], George Z. Papageorgiou [b], Dimitrios N. Bikiaris [a]

From the journal:
Polymer Chemistry

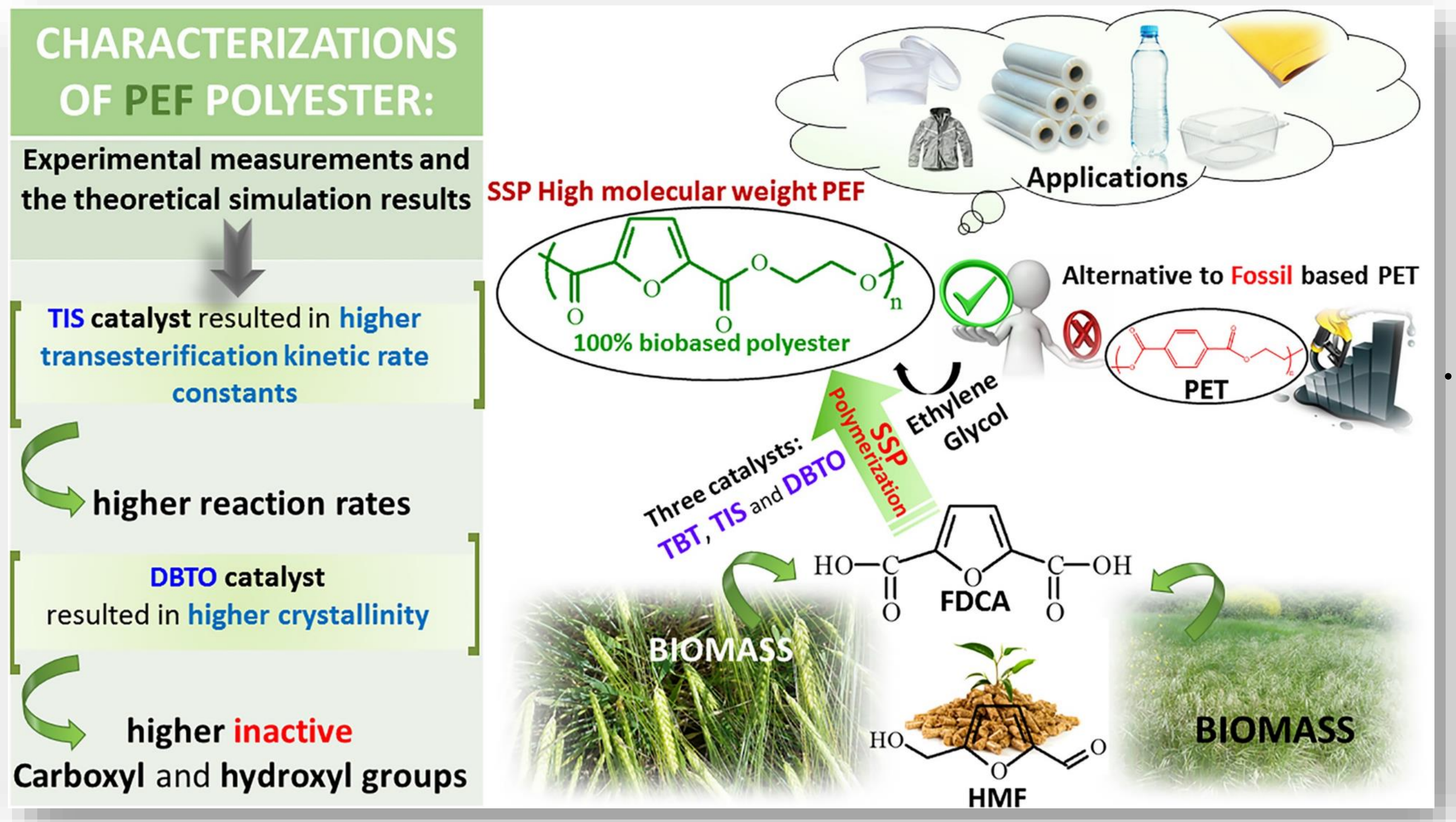
LINK

Effect of catalyst type on molecular weight increase and coloration of poly(ethylene furanoate) biobased polyester during melt polycondensation†

Check for updates

Zoe Terzopoulou, [a] Elisavet Karakatsianopoulou, [a] Nejib Kasmi, [a] Vasileios Tsanaktsis, [a] Nikolaos Nikolaidis, [a] Margaritis Kostoglou, [b] George Z. Papageorgiou, [c] Dimitra A. Lambropoulou [d] and Dimitrios N. Bikiaris *[a]

Effect **of catalyst type on molecular weight increase** of PEF during **SSP**



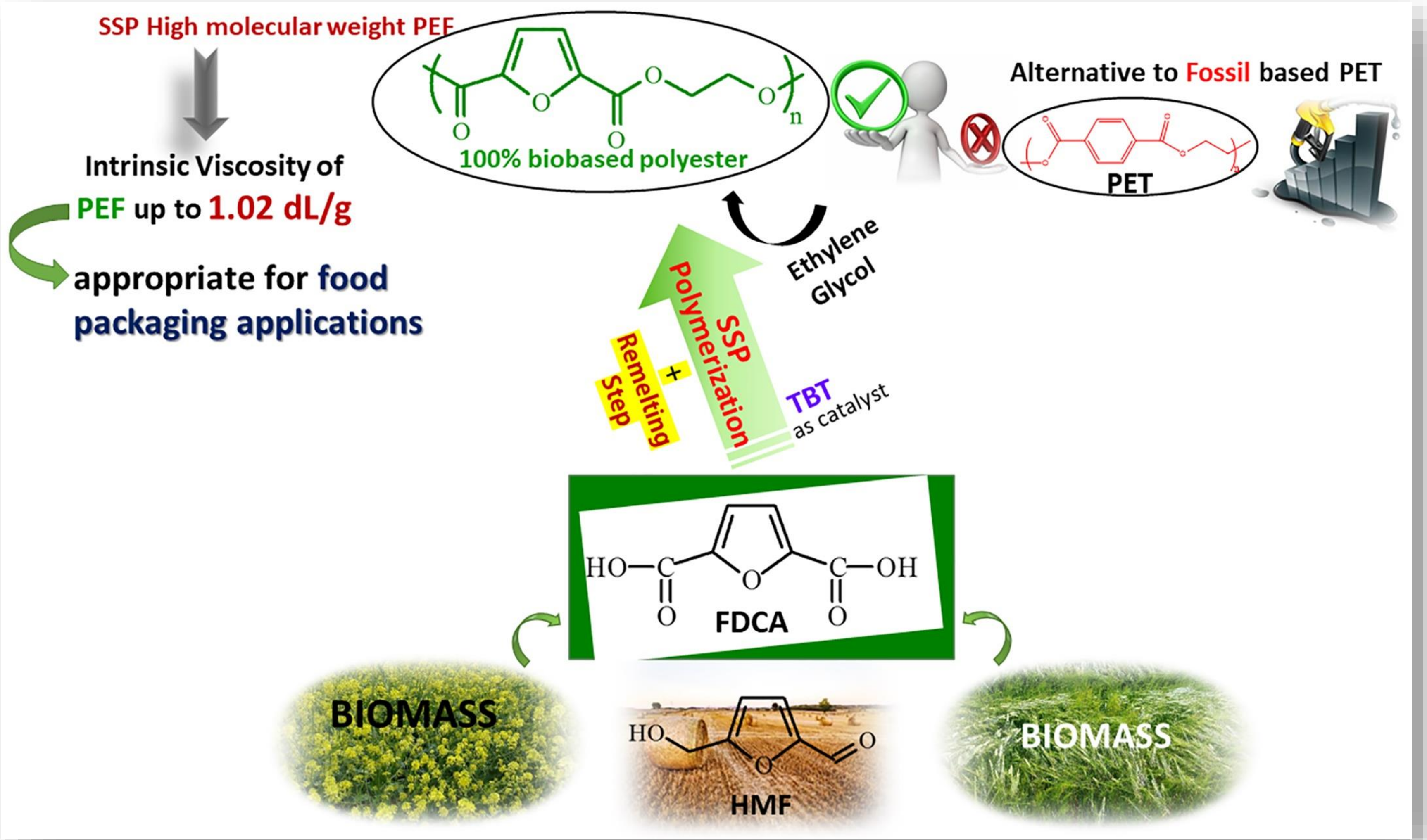
- Three different catalysts:
  - ❑ tetrabutyl titanate (**TBT**)
  - ❑ titanium(IV) isopropoxide (**TIS**)
  - ❑ dibutyltin(IV) oxide (**DBTO**)

- Solid-state polymerization (SSP) was conducted at different reaction times (1, 2, 3.5, and 5 h) and temperatures 190, 200, and 205°C, under vacuum.

  - SSP time and temperature
  - IV and MW

N. Kasmi, M. Majdoub, G.Z. Papageorgiou*, D.S. Achilias, D.N. Bikiaris*. Solid-state polymerization of poly(ethylene furanoate) biobased polyester, I: Effect of catalyst type on molecular weight increase, *Polymers (Q1)* **2017**, *9*, 607 (LINK)

An Efficient and Facile Method to Synthesize, through SSP, **High Molecular Weight PEF** Polyester Appropriate for Food Packaging Applications



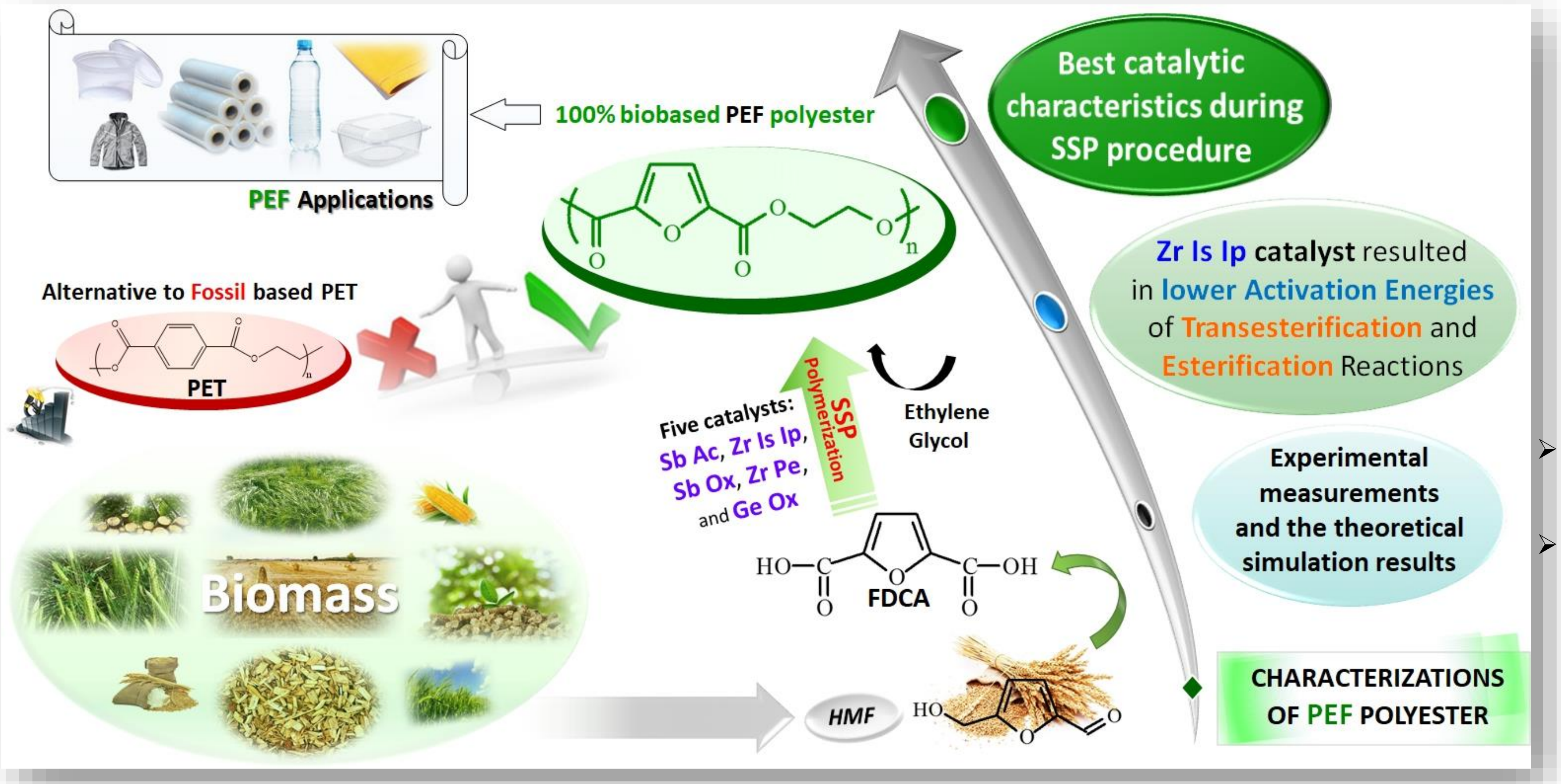
- This work is the first study which investigated the feasibility of SSP **after remelting process** to synthesize high molecular weight PEF, which could be applicable in food packaging applications.

- Remelting process resulted in a higher increase of the polymerization rate

- Very high molecular weight PEF

N. Kasmi, G.Z. Papageorgiou*, D.S. Achilias, D.N. Bikiaris*. Solid-State Polymerization of Poly(Ethylene Furanoate) Biobased Polyester, II: An Efficient and Facile Method to Synthesize High Molecular Weight Polyester Appropriate for Food Packaging Applications, *Polymers (Q1)* **2018**, *10*, 471 (LINK)

Extended study on **Effect of catalyst type on molecular weight increase** of PEF during SSP



- Five different catalysts:
  - antimony acetate (III) (**Sb Ac**)
  - zirconium (IV) isopropoxide isopropanal (**Zr Is Ip**)
  - antimony (III) oxide (**Sb Ox**)
  - zirconium (IV) 2,4-pentanedionate (**Zr Pe**)
  - germanium (IV) oxide (**Ge Ox**)

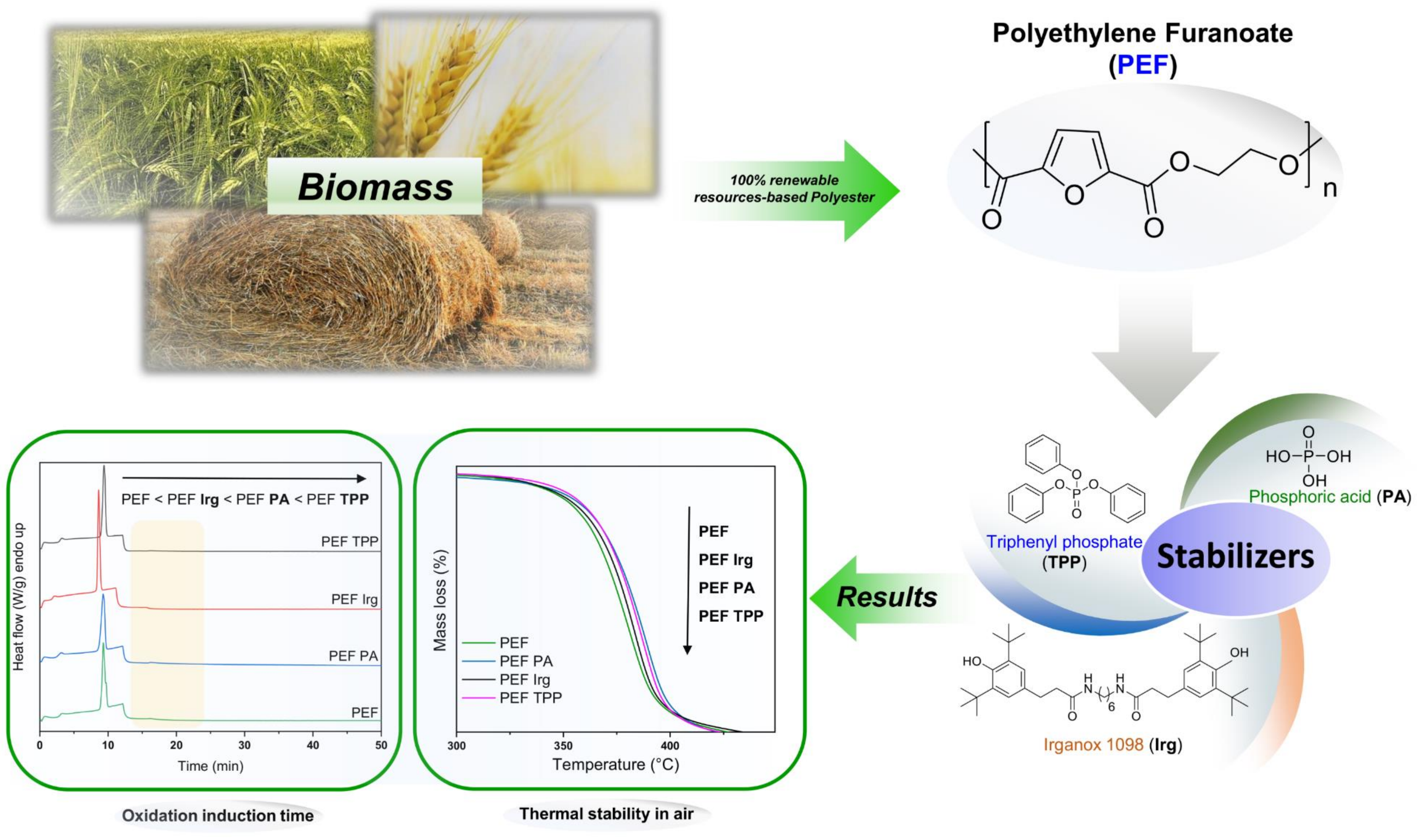
- **Zr Is Ip** catalyst shows the best catalytic characteristics

#

- **Ge Ox** catalyst resulted in the highest activation energies, thus leading to lower molecular weight PEF

Y. Chebbi, **N. Kasmi**, M. Majdoub, G.Z. Papageorgiou*, D.N. Achilias, D.N. Bikiaris*. Solid-State Polymerization of Poly(Ethylene Furanoate) Biobased Polyester, III: Extended Study on Effect of Catalyst Type on Molecular Weight Increase, *Polymers (Q1)* **2019**, *11*, 438 (LINK)

Effect of **additives on the thermal and thermo-oxidative stability** of PEF biobased polyester



- PEF stabilizers have been studied for first time.
- Phenolic antioxidant (Irganox 1098) and two phosphorus-containing thermal stabilizers have been evaluated

It was found that:

All the stabilizers;

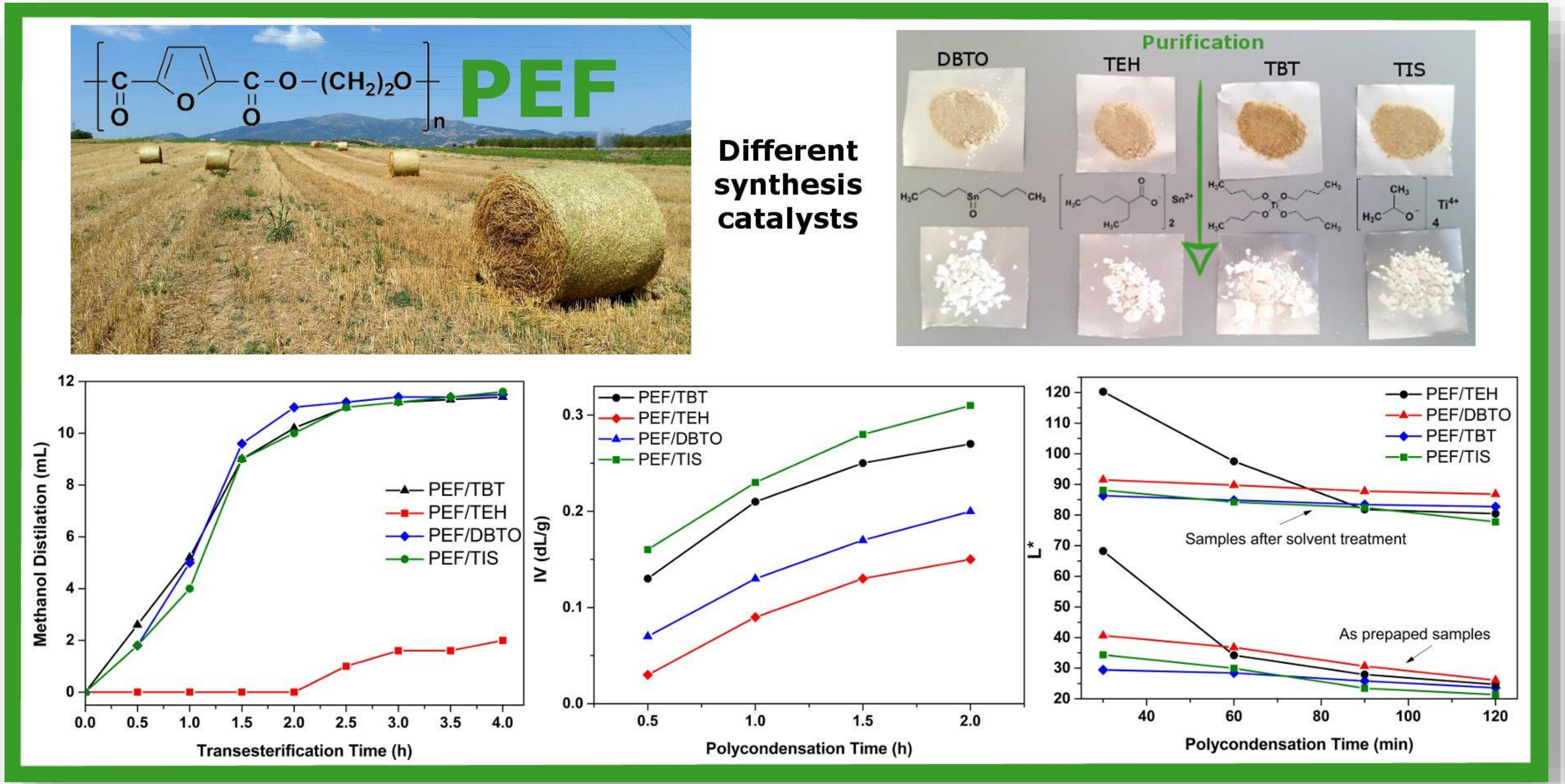
- slightly improved the thermal stability of PEF in inert and oxidative atmosphere
- increased the oxidation induction time
- slightly reduced the % crystallinity.

➢ Triphenyl phosphate was the most efficient stabilizer.

The stabilizers can successfully decelerate the thermal degradation and physical aging of PEF in very small quantities, with the P-containing ones PA and mainly TPP being the most effective.

Z. Terzopoulou, M. Wahbi, **N. Kasmi**, G.Z. Papageorgiou, D.N. Bikiaris*. Effect of additives on the thermal and thermo-oxidative stability of poly(ethylene furanoate) biobased polyester, *Thermochim. Acta (Q1)* **2020**, *686,* 178549 (LINK)

Effect of **catalyst type on molecular weight increase and coloration** of PEF biobased polyester during melt polycondensation



- tetrabutyl titanate (**TBT**)
- titanium(IV) isopropoxide (**TIS**)
- tin(II)2-ethylhexanoate (**TEH**)
- dibutyltin(IV) oxide (**DBTO**)

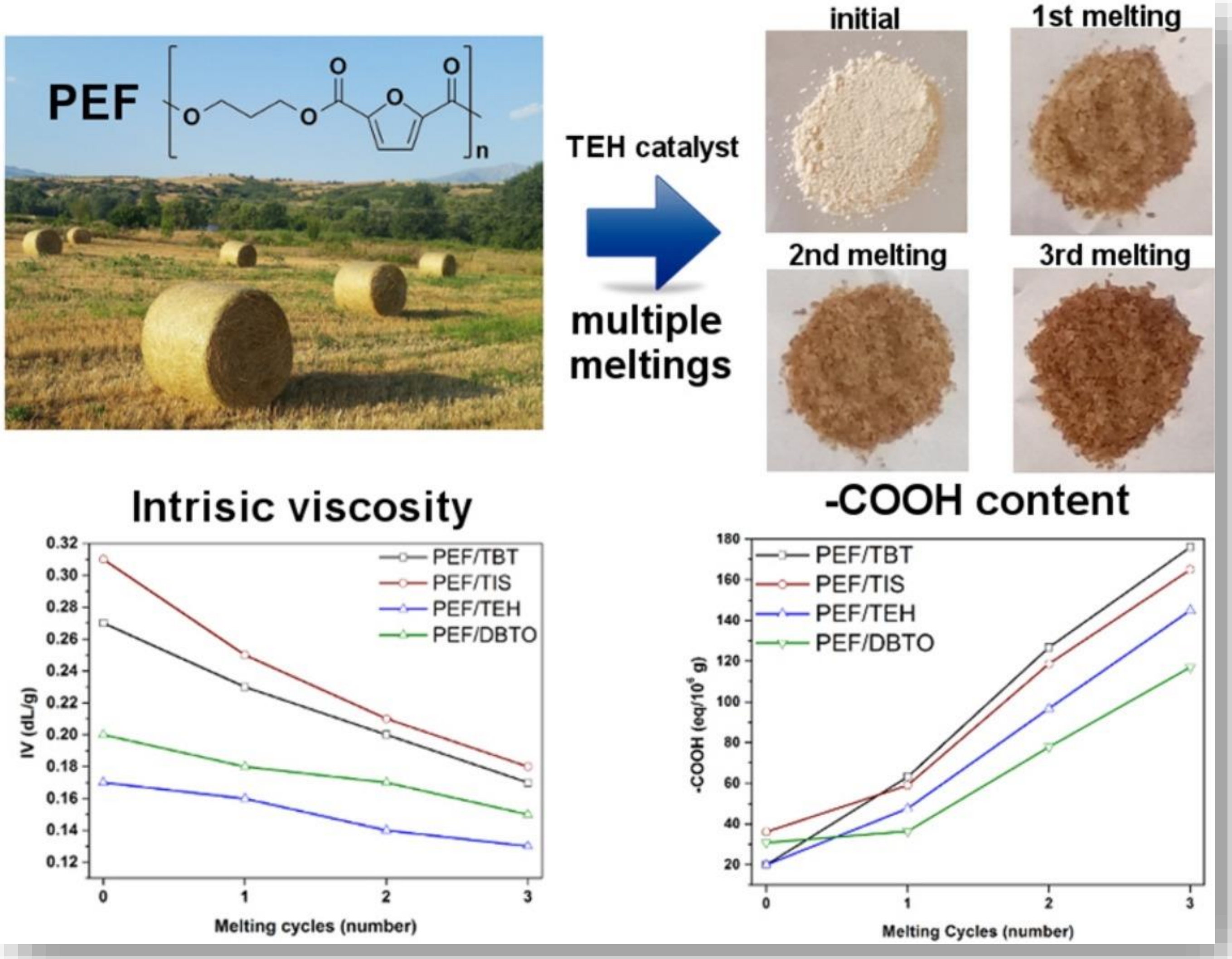
It was found that:

- ✓ The catalysts used affected both the transesterification and melt polycondensation reactions during synthesis of PEF.
- ✓ Titanate catalysts TBT and mainly TIS were found to be the most effective ones (MW), compared with tin catalysts like TEH and DBTO, which have the lowest reactivity
- ✓ Titanate catalysts lead to the highest coloration.
- ✓ Polycondensation time affected the colouration, colour intensity was increased progressively by increasing polycondensation time.

This is due to the decomposition of by-products

Z. Terzopoulou, E. Karakatsianopoulou, **N. Kasmi**, V. Tsanaktsis, N. Nikolaidis, M. Kostoglou, G.Z. Papageorgiou, D.A. Lambropoulou, D.N. Bikiaris*. Effect of catalyst type on molecular weight increase and coloration of poly(ethylene furanoate) biobased polyester during melt polycondensation, *Polym. Chem. (Q1)* **2017**, *8*, 6895-6908 (LINK)

Effect of **catalyst type on recyclability and decomposition mechanism** of PEF biobased polyester



- tetrabutyl titanate (**TBT**)
- titanium(IV) isopropoxide (**TIS**)
- tin(II)2-ethylhexanoate (**TEH**)
- dibutyltin(IV) oxide (**DBTO**)

It was found that:

- ✓ IV values continuously decrease by increasing remelting cycles, while -COOH end group numbers have the opposite trend.
- ✓ with **titanate** catalysts accelerating PEF decomposition at a higher extent that **tin** catalysts.
- ✓ The molecular weight decrease causes a substantial increase in the degree of crystallinity of the remelted samples, while the thermal stability is decreased.
- ✓ The decomposition of polyesters synthesized with titanium catalysts (TBT and TIS) takes place mainly via heterolytic routes (β-hydrogen scission).

  #

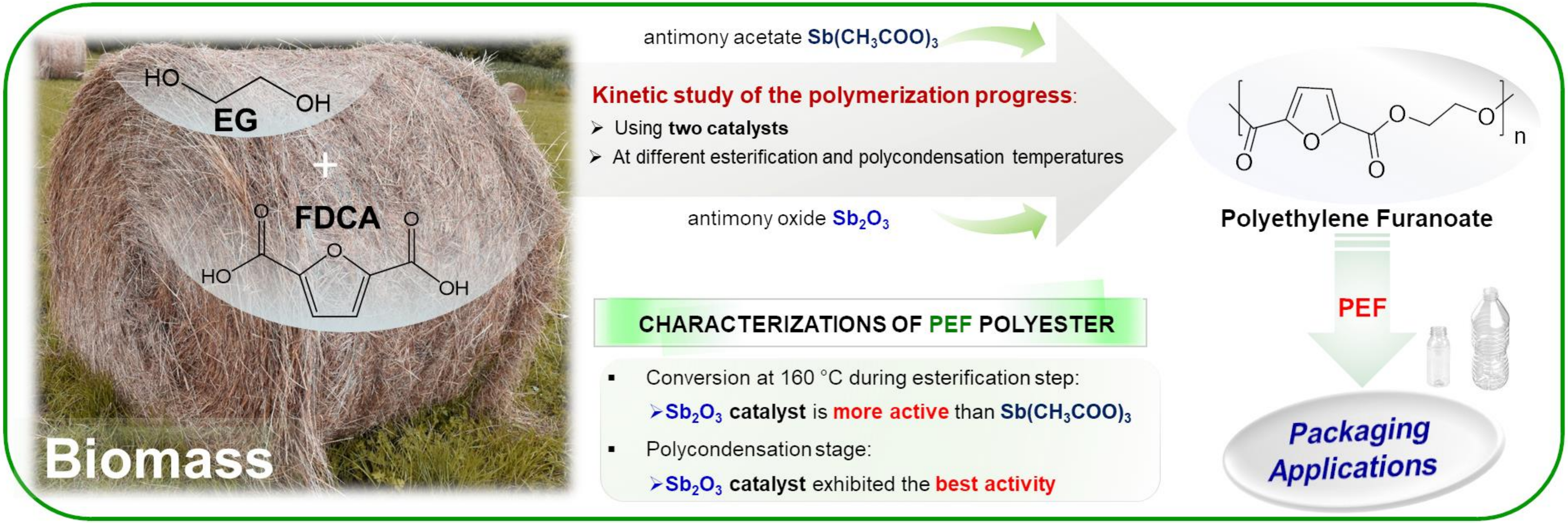
  In the samples with TEH and DBTO, homolytic scission is more extensive.

➢ Thermal Degradation mechanism study (Pyrolysis-GC/MS):

Identification of pyrolysis products → producing mainly vinyl and carboxyl end groups

Z. Terzopoulou, E. Karakatsianopoulou, **N. Kasmi**, M. Majdoub, G.Z. Papageorgiou, D.N. Bikiaris*. Effect of catalyst type on recyclability and decomposition mechanism of poly(ethylene furanoate) biobased polyester, *J. Anal. Appl. Pyrolysis (Q1)* **2017**, *126*, 357-370 (LINK)

An in-depth kinetic study of the polymerization of high-purity FDCA with ethylene glycol (EG) with two different catalysts and at three different temperatures



L. Papadopoulos, A. Zamboulis, **N. Kasmi**, M. Wahbi, C. Nannou, D. A. Lambropoulou, M. Kostoglou, G.Z. Papageorgiou, D.N. Bikiaris*. Investigation of the catalytic activity and reaction kinetic modeling of two antimony catalysts in the synthesis of poly(ethylene furanoate), *Green Chemistry (Q1)* **2021**, *23,* 2507-2524 (LINK).

3. Furanoate Polyurethanes and other sustainable materials

materials MDPI

LINK

Article

Synthesis and Characterization of Bio-Based Polyesters: Poly(2-methyl-1,3-propylene-2,5-furanoate), Poly(isosorbide-2,5-furanoate), Poly(1,4-cyclohexanedimethylene-2,5-furanoate)

Zoi Terzopoulou [1], Nejib Kasmi [1], Vasilios Tsanaktsis [1], Nikolaos Doulakas [1], Dimitrios N. Bikiaris [1,*], Dimitris S. Achilias [1] and George Z. Papageorgiou [2,*]

European Polymer Journal
Volume 112, March 2019, Pages 1-14

Sustainable thermoplastics from renewable resources: Thermal behavior of poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate)

LINK

Nejib Kasmi [a], Niki Poulopoulou [b], Zoi Terzopoulou [a], Dimitrios G. Papageorgiou [c], Dimitrios N. Bikiaris [a], George Z. Papageorgiou [b]

molecules MDPI

LINK

Article

Thermal Decomposition Kinetics and Mechanism of In-Situ Prepared Bio-Based Poly(propylene 2,5-furan dicarboxylate)/Graphene Nanocomposites

Zoi Terzopoulou [1], Evangelia Tarani [2], Nejib Kasmi [1], Lazaros Papadopoulos [1], Konstantinos Chrissafis [2,*], Dimitrios G. Papageorgiou [3], George Z. Papageorgiou [4] and Dimitrios N. Bikiaris [1,*]

Biomacromolecules

pubs.acs.org/Biomac

Isocyanate-Free Fully Biobased Star Polyester-Urethanes: Synthesis and Thermal Properties

LINK

Baptiste Quienne, Nejib Kasmi, Reiner Dieden, Sylvain Caillol, and Youssef Habibi*

Cite This: *Biomacromolecules* 2020, 21, 1943–1951

International Journal of Biological Macromolecules
Volume 214, 1 August 2022, Pages 128-139

Effect of the structural features of biobased linear polyester plasticizers on the crystallization of polylactides

LINK

Maryam Safari [a, 1], Nejib Kasmi [b, 1, 2], Carla Pisani [b], Vincent Berthé [b], Alejandro J. Müller [a, c], Youssef Habibi [b]

Polymer Degradation and Stability
Volume 181, November 2020, 109315

Effective and facile solvent-free synthesis route to novel biobased monomers from vanillic acid: Structure–thermal property relationships of sustainable polyesters

Nejib Kasmi [a], Lazaros Papadopoulos [a], Yosra Chebbi [a], George Z. Papageorgiou [b], Dimitrios N. Bikiaris [a]

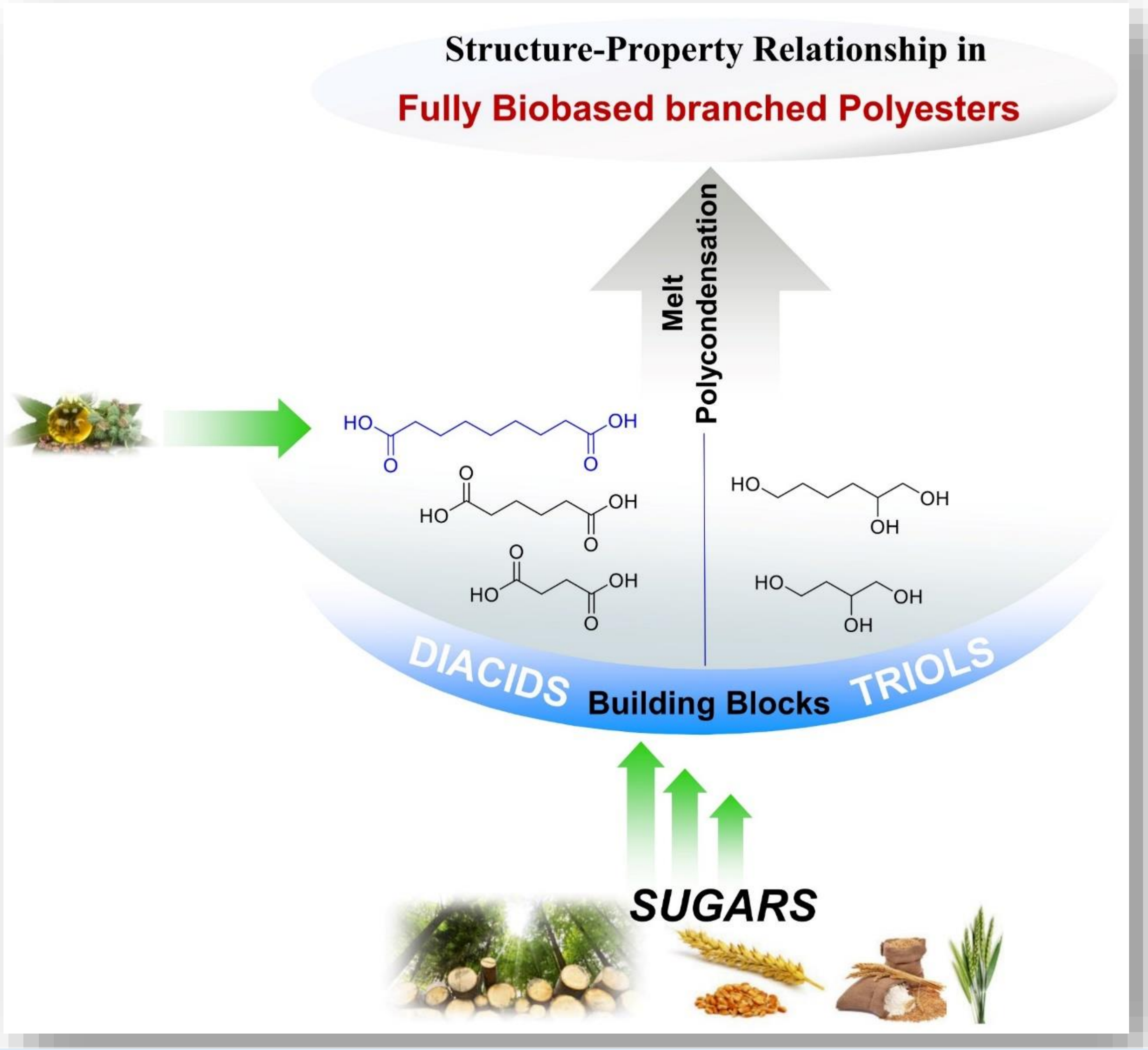
From the journal:
Polymer Chemistry

Synthesis and characterization of fully biobased polyesters with tunable branched architectures†

LINK

Nejib Kasmi, [a] Catherine Pinel, [b] Denilson Da Silva Perez, [c] Reiner Dieden [a] and Youssef Habibi *[a]

Synthesis and characterization of new fully biobased polyesters with tunable branched architectures



6 Branched polyesters

bearing Carboxyl end groups

- ✓ Good thermal stability with 168 °C < $T_{d,5\%}$ < 236 °C
- ✓ Wide T_g range: -57 °C < T_g < -18 °C
- ✓ Wholly amorphous materials

6 Branched polyesters

bearing Hydroxyl end groups

- ✓ Good resistance to heat with 180 °C < $T_{d,5\%}$ < 268 °C
- ✓ Very wide T_g range: -37 °C < T_g < 19 °C
- ✓ Wholly amorphous materials

Intermediate substrates for:

- chain extension
- Crosslinking
- co-polymerization

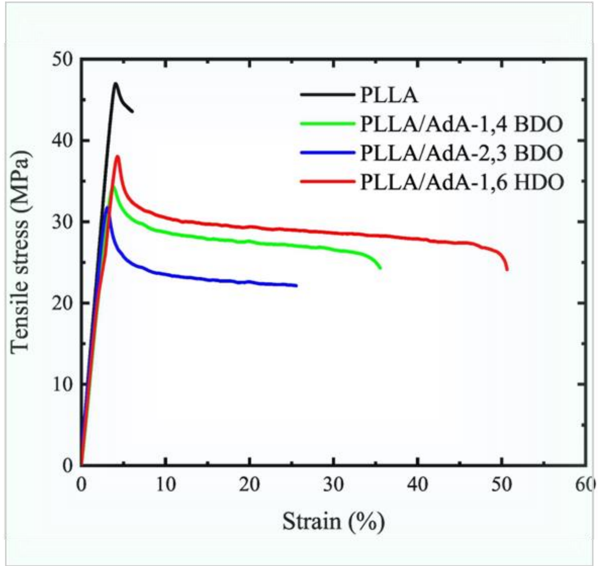
High-performance eco-friendly materials with broad application domains

N. Kasmi, C. Pinel, D. Da Silva Perez, R. Dieden, Y. Habibi. Synthesis and characterization of fully biobased polyesters with tunable branched architectures, *Polymer Chemistry (Q1)* **2021**,*12*, 991-1001 (LINK)

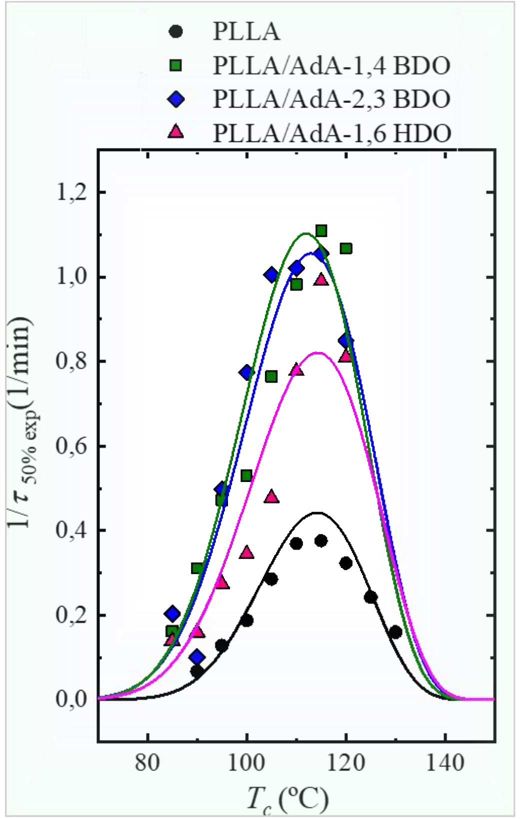
New 100% biobased polyester plasticizers derived from adipic acid (AdA) were successfully employed, for the first time, to accelerate the crystallization rate and enhance the mechanical properties of polylactide (PLLA); an important step to improve its performance and expand its range of applications

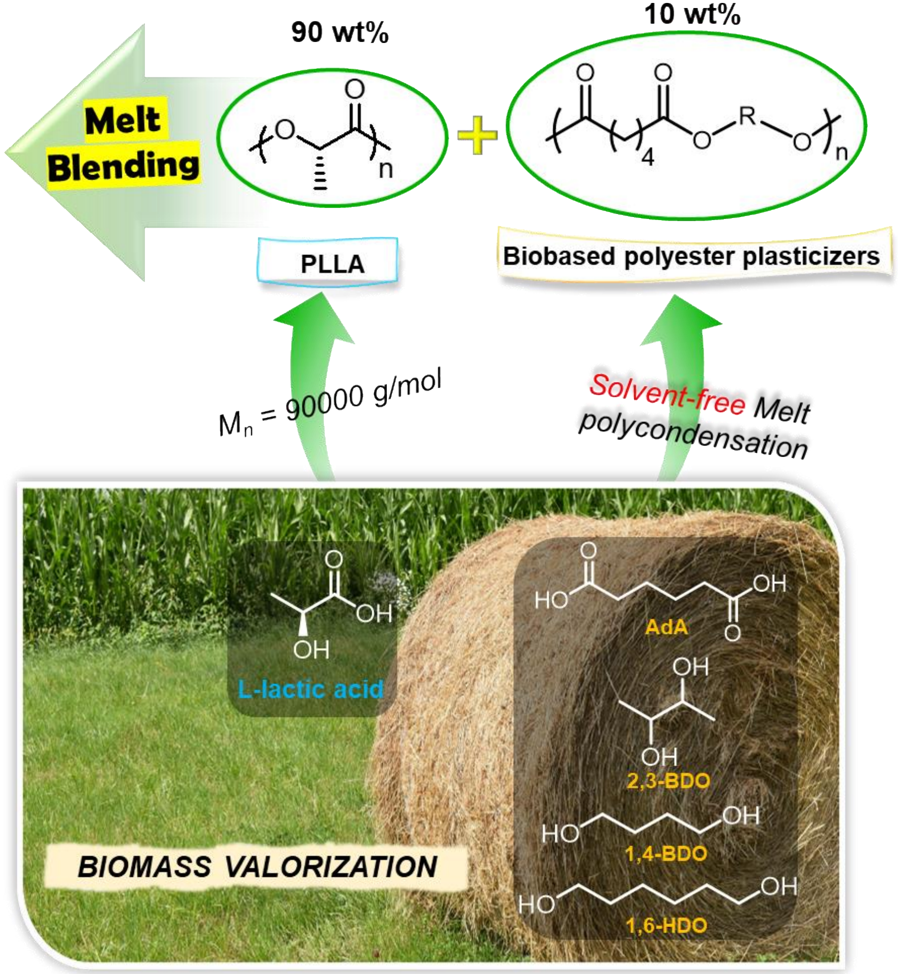
The addition of AdA-based plasticizers to PLLA:

- *decreases* T_g *by up to* ***11 ºC***
- *significantly increases the elongation at break by about* ***8 times*** *compared with neat PLLA*
- *increases the nucleation rate from the glassy state by around* ***50-110 %***
- *causes a* ***remarkable increase in the overall crystallization rate*** *from the glassy state which was* ***2-3 times*** *faster for the plasticized PLLAs than neat PLLA*



Such findings make these aliphatic polyester plasticizers derived from biomass very promising for improving the properties and applications of PLA



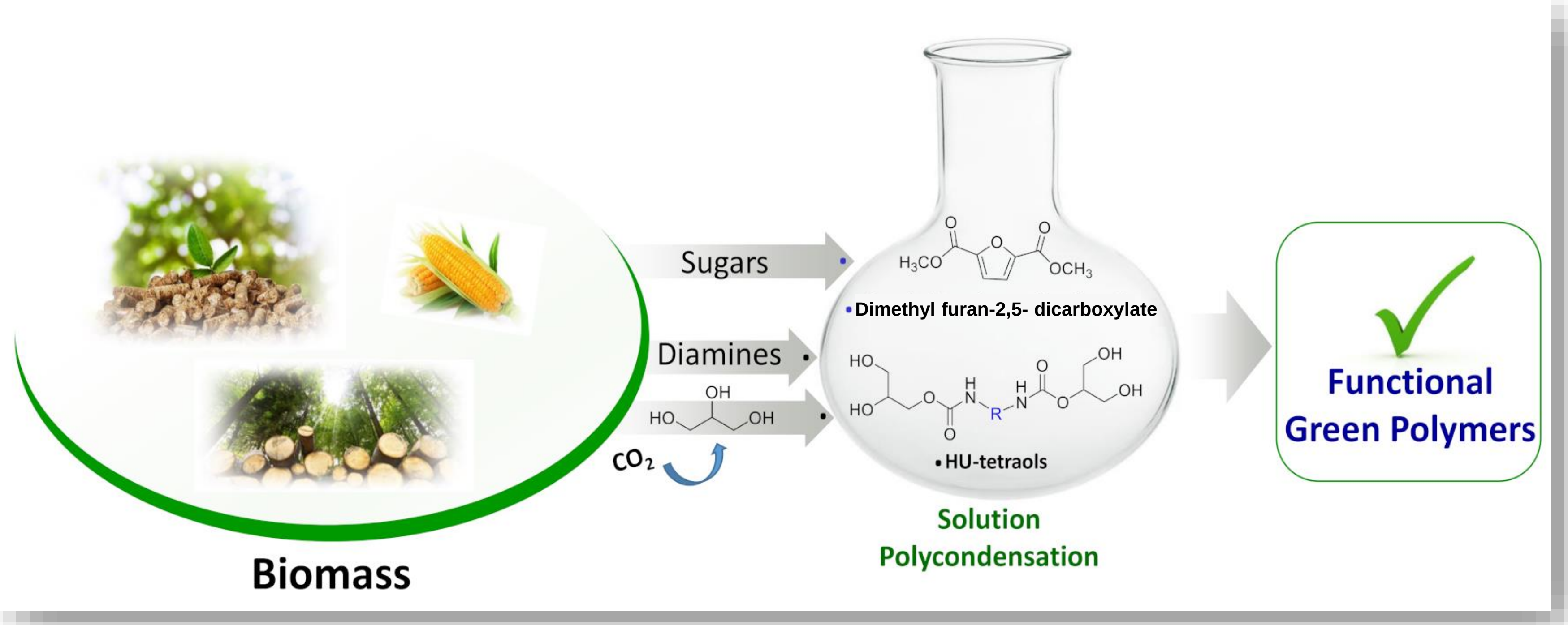


M. Safari,[a] **N. Kasmi**,[a] C. Pisani, V. Berthé, A. J. Muller, Y. Habibi, Y. Habibi. Effect of the structural features of biobased linear polyester plasticizers on the crystallization of polylactides, *International Journal of Biological Macromolecules (Q1)* **2022**, *214*, 128-139 (LINK)

[a] equal contribution

A green strategy for the synthesis of **fully biobased** isocyanate-free polyester-urethanes (NIPHEUs) was developed

- These materials were synthesized by step-growth polymerization combining sugar-derived dimethyl-2,5-furan dicarboxylate with polyhydroxylurethanes adducts bearing four hydroxyl groups (**HU-tetraols**).



Glycerol + CO_2 → Glycerol carbonate

Diamines: 1,8-diaminooctane, 1,12-diaminododecane

Furanoate Isocyanate-free polyester-urethanes

- ✓ Satisfactory thermal stability (170°C < $T_{d,5\%}$ < 220°C)
- ✓ High melting temperatures (93°C < T_m < 110°C)

- The resulting networks exhibited striking thermal behavior upon repetitive heating cycles.

✓ This is related to a thermal-induced bond exchange probably driven by transcarbamoylation reaction.

Such interesting vitrimer-like behavior for this new type of NIPHEUs is unique

Pave the way toward the design of a new range of functional green materials

B. Quienne, **N. Kasmi**, R. Dieden, S. Caillol, Y. Habibi*. Isocyanate-free fully biobased star polyester-urethanes: synthesis and thermal properties, *Biomacromolecules (Q1)*, **2020**, *21*, 1943–1951 (LINK)

It was described as one of the "**grand challenges**" facing chemists

CHALLENGE

Solvent-free synthesis of monomers is one among the most promising ways to develop greener polymers

Solution

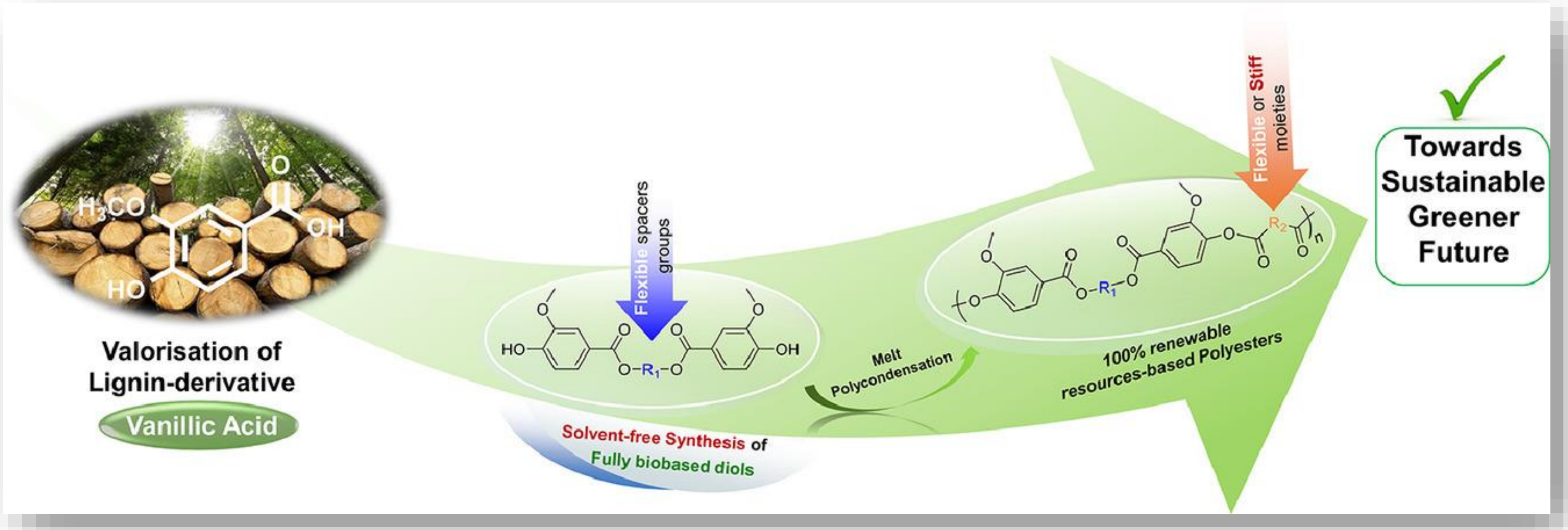
A truly efficient, practical, and more greener solvent-free synthetic route was successfully applied to prepare for first time three novel **100% renewable resources-based** diols derived from **vanillic acid**

New Monomers

- Excellent thermal stability
- High melting points (121 °C - 142 °C)

Polyesters

- high thermal stability ($314°C < T_{d,5\%} < 373$ °C)
- A very wide glass transition temperatures (-2.8 °C – 69 °C)

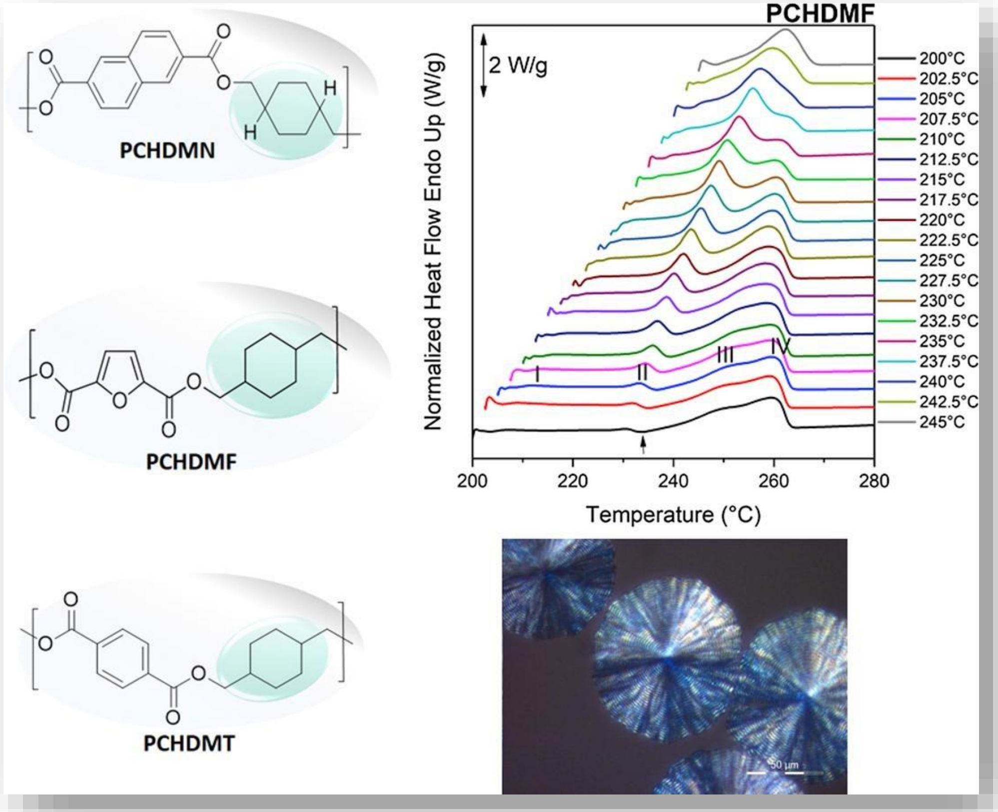


N. Kasmi, L. Papadopoulos, Y. Chebbi, G.Z. Papageorgiou, D.N. Bikiaris*. Effective and facile solvent-free synthesis route to novel biobased monomers from vanillic acid: Structure-thermal property relationships of sustainable polyesters, Polym. Degrad. Stab. *(Q1)* **2020**, *181*, 109315 (LINK)

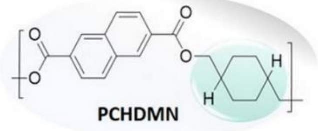
An **in-depth** study on the thermal behaviour of Poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate)

renewable feedstock-based PCHDMF thermoplastic

petroleum-based resources analogues



eXPRESS Polymer Letters Vol.12, No.3 (2018) 227–23
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2018.21



Poly(1,4-cyclohexanedimethylene 2,6-naphthalate) polyester with high melting point: Effect of different synthesis methods on molecular weight and properties

N. Kasmi[1], Z. Terzopoulou[1], G. Z. Papageorgiou[2], D. N. Bikiaris[1]*

[1]Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece
[2]Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece

Received 9 August 2017; accepted in revised form 19 October 2017

Abstract. In the current manuscript, a new approach for the synthesis of poly(1,4- cyclohexanedimethylene 2,6-naphthalate) (PCHDMN) derived from dimethyl 2,6-naphthalenedicarboxylate (2,6-DMN) and 1,4-Cyclohexanedimethanol (CHDM) via melt polycondensation method is introduced. The effect of three different synthesis pathways, polycondensation time and temperature on polyesters molecular weight increase has been investigated. All of the prepared samples were characterized measuring their intrinsic viscosity (IV), thermal properties and morphology with differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD), respectively. The results demonstrated the effectiveness of the synthesis pathway proposed for the preparation of PCHDMN, resulting in high molecular weight (IV value around 0.5 dL/g) and much shorter reaction time. Melt polycondensation temperatures above melting point of polyester should be avoided to be used due to the decomposition of polyester. This was proved by thermogravimetric analysis (TGA) and Pyrolysis-gas chromatography–mass spectroscopy analysis (Py-GC/MS).

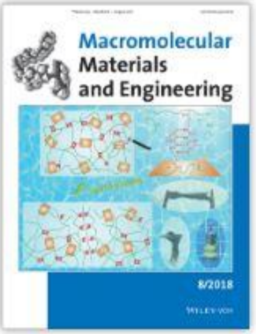
N. Kasmi, N. Poulopoulou, Z. Terzopoulou, D.G. Papageorgiou*, D.N. Bikiaris, G.Z. Papageorgiou*. Sustainable Thermoplastics from Renewable Resources: Thermal behavior of Poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate), *Eur. Polym. J. (Q1)* **2019**, *112,* 1-14 (LINK)

N. Kasmi, Z. Terzopoulou, G.Z. Papageorgiou, D.N. Bikiaris*. Poly(1,4-cyclohexanedimethylene 2,6-naphthalate) polyester with high melting point: effect of different synthesis methods on molecular weight and properties, *eXPRESS Polym. Lett. (Q1)* **2018**, *12*, 227-237 (LINK)

4. Furan-based Polyester Blends

Macro-molecular Materials and Engineering
Open Access

LINK



Volume 303, Issue 8
August 2018
1800153

Communication

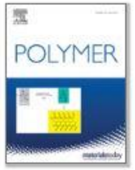
Sustainable Polymers from Renewable Resources: Polymer Blends of Furan-Based Polyesters

Niki Poulopoulou, Nejib Kasmi, Dimitrios N. Bikiaris, Dimitrios G. Papageorgiou, George Floudas, George Z. Papageorgiou

First published: 27 May 2018 | https://doi.org/10.1002/mame.201800153 | Citations: 38

ELSEVIER

Polymer
Volume 174, 12 June 2019, Pages 187-199



Green polymeric materials: On the dynamic homogeneity and miscibility of furan-based polyester blends

Niki Poulopoulou [a], Achilleas Pipertzis [b], Nejib Kasmi [c], Dimitrios N. Bikiaris [c], Dimitrios G. Papageorgiou [d], George Floudas [b], George Z. Papageorgiou [a]

LINK

Open Access | Editor's Choice | Article

Exploring Next-Generation Engineering Bioplastics: Poly(alkylene furanoate)/Poly(alkylene terephthalate) (PAF/PAT) Blends

by Niki Poulopoulou [1], Nejib Kasmi [2], Maria Siampani [1], Zoi N. Terzopoulou [2], Dimitrios N. Bikiaris [2], Dimitris S. Achilias [2], Dimitrios G. Papageorgiou [3,*] and George Z. Papageorgiou [1,*]

1 Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
2 Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece
3 School of Materials and National Graphene Institute, University of Manchester, Oxford Road, Manchester M13 9PL, UK
* Authors to whom correspondence should be addressed.

Polymers **2019**, *11*(3), 556; https://doi.org/10.3390/polym11030556

LINK

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polymers

MDPI

Article

A New Era in Engineering Plastics: Compatibility and Perspectives of Sustainable Alipharomatic Poly(ethylene terephthalate)/Poly(ethylene 2,5-furandicarboxylate) Blends

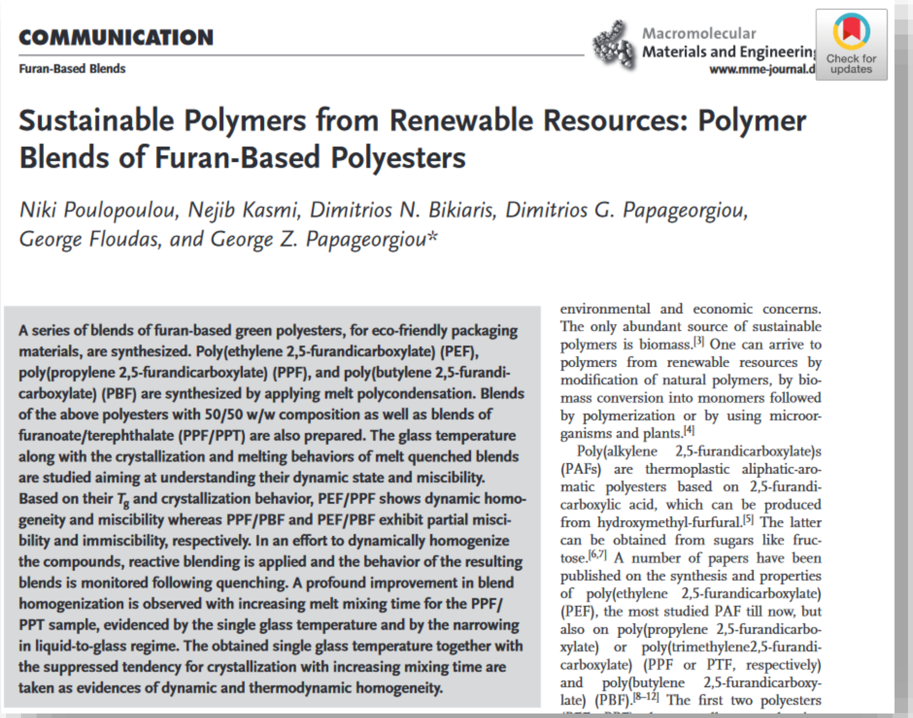
Dimitrios G. Papageorgiou [1,*], Irini Tsetsou [2], Raphael O. Ioannidis [2], George N. Nikolaidis [2], Stylianos Exarhopoulos [3], Nejib Kasmi [4], Dimitrios N. Bikiaris [5], Dimitris S. Achilias [5] and George Z. Papageorgiou [2,6,*]

LINK

➢ Three different series of novel fully biobased furan-based polyester blends were prepared for the **first time**;

- **PEF-PPF 50-50** (dynamic homogeneity and miscibility)
- **PBF-PPF 50-50** (partial miscibility)
- **PEF-PBF 50-50** (partial immiscibility)

❑ Poly(ethylene 2,5-furandicarboxylate) (**PEF**)
❑ poly(propylene 2,5-furandicarboxylate) (**PPF**)
❑ poly(butylene 2,5-furandicarboxylate) (**PBF**)


COMMUNICATION

Furan-Based Blends

Macromolecular Materials and Engineering
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Sustainable Polymers from Renewable Resources: Polymer Blends of Furan-Based Polyesters

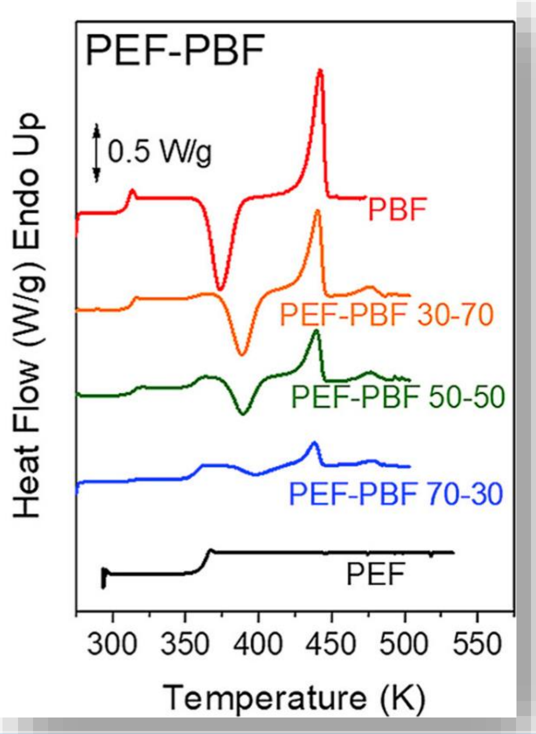
*Niki Poulopoulou, Nejib Kasmi, Dimitrios N. Bikiaris, Dimitrios G. Papageorgiou, George Floudas, and George Z. Papageorgiou**

A series of blends of furan-based green polyesters, for eco-friendly packaging materials, are synthesized. Poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), and poly(butylene 2,5-furandicarboxylate) (PBF) are synthesized by applying melt polycondensation. Blends of the above polyesters with 50/50 w/w composition as well as blends of furanoate/terephthalate (PPF/PPT) are also prepared. The glass temperature along with the crystallization and melting behaviors of melt quenched blends are studied aiming at understanding their dynamic state and miscibility. Based on their T_g and crystallization behavior, PEF/PPF shows dynamic homogeneity and miscibility whereas PPF/PBF and PEF/PBF exhibit partial miscibility and immiscibility, respectively. In an effort to dynamically homogenize the compounds, reactive blending is applied and the behavior of the resulting blends is monitored following quenching. A profound improvement in blend homogenization is observed with increasing melt mixing time for the PPF/PPT sample, evidenced by the single glass temperature and by the narrowing in liquid-to-glass regime. The obtained single glass temperature together with the suppressed tendency for crystallization with increasing mixing time are taken as evidences of dynamic and thermodynamic homogeneity.

environmental and economic concerns. The only abundant source of sustainable polymers is biomass.[3] One can arrive to polymers from renewable resources by modification of natural polymers, by biomass conversion into monomers followed by polymerization or by using microorganisms and plants.[4]

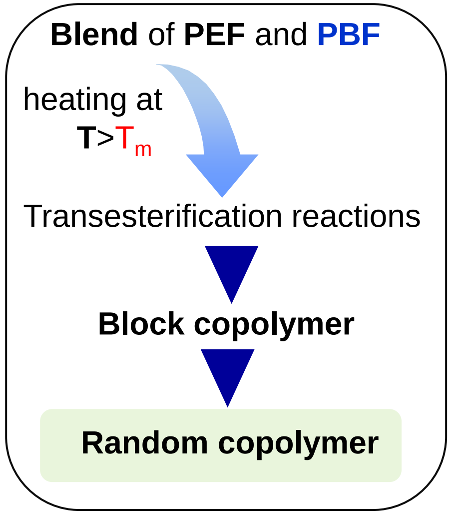
Poly(alkylene 2,5-furandicarboxylate)s (PAFs) are thermoplastic aliphatic-aromatic polyesters based on 2,5-furandicarboxylic acid, which can be produced from hydroxymethyl-furfural.[5] The latter can be obtained from sugars like fructose.[6,7] A number of papers have been published on the synthesis and properties of poly(ethylene 2,5-furandicarboxylate) (PEF), the most studied PAF till now, but also on poly(propylene 2,5-furandicarboxylate) or poly(trimethylene2,5-furandicarboxylate) (PPF or PTF, respectively) and poly(butylene 2,5-furandicarboxylate) (PBF).[8–12] The first two polyesters

N. Poulopoulou, **N. Kasmi**, D.N. Bikiaris, D.G. Papageorgiou, G. Floudas, G.Z. Papageorgiou*. Sustainable polymers from renewable resources: Polymer blends of furan-based polyesters, *Macromol. Mater. Eng. (Q1)* **2018**, 1800153 (LINK)



N. Poulopoulou, A. Pipertzis, **N. Kasmi**, D.N. Bikiaris, D.G. Papageorgiou, G. Floudas, G.Z. Papageorgiou*. Green polymeric materials: On the dynamic homogeneity and miscibility of furan-based polyester blends, *Polymer (Q1)* **2019**, *174*, 187-199 (LINK)

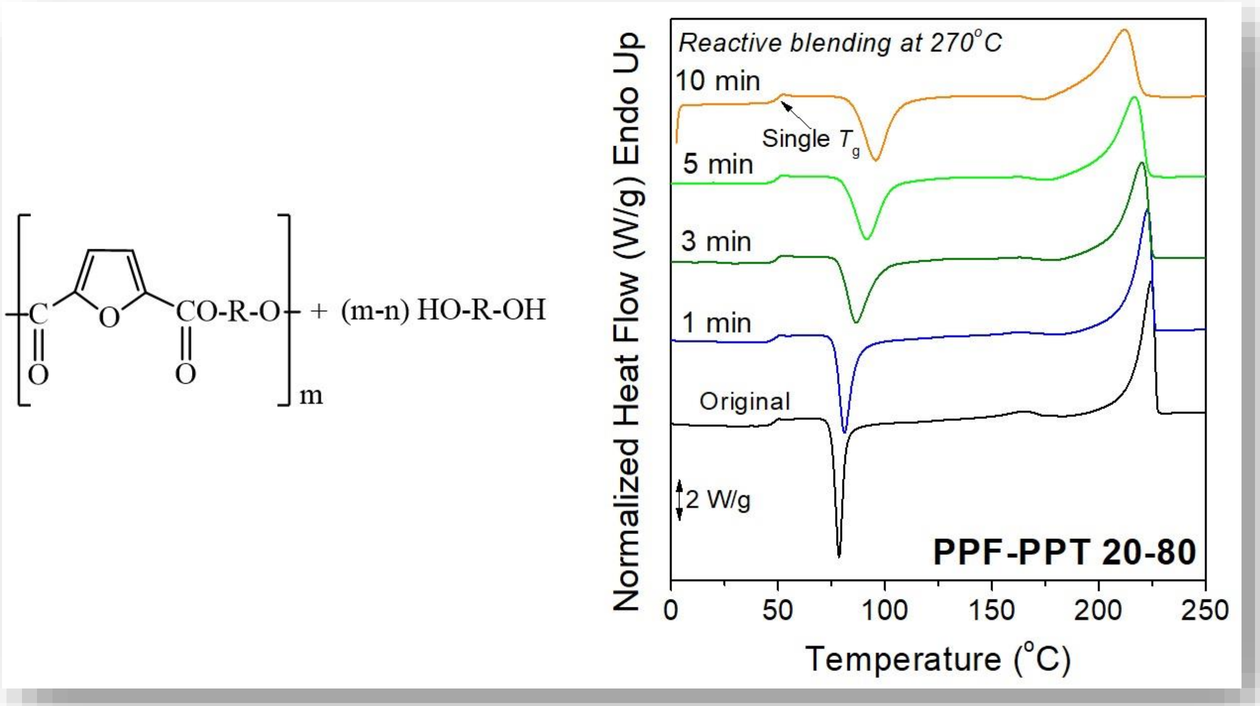
- The blends are dynamically homogeneous when the backbones differ by a single methylene unit.
- Reactive blending promotes thermodynamic miscibility of the furanoate-based homopolymers.
- After reactive blending, a copolymer was formed, making the blend dynamically homogeneous:



Evaluation whether **poly(alkylene furanoate)s** can successfully form blends with **poly(alkylene terephthalate)s**

✓ Three different types of blends with different compositions¨:

- ❑ poly(ethylene furanoate)/poly(ethylene terephthalate) (**PEF/PET**)
- ❑ poly(propylene furanoate)/poly(propylene terephthalate) (**PPF/PPT**)
- ❑ poly(1,4-cyclohenedimethylene furanoate)/poly(1,4-cycloxehane terephthalate) (**PCHDMF/PCHDMT**)



It was found that:

➢ **PEF/PET** and **PPF/PPT** blends

Reactive Blending — heating at **T**>T_m

(**PETF**) and (**PPTF**) random copolyesters

Immiscibility and compatibility of the individual components of the blends

N. Poulopoulou, **N. Kasmi**, M. Siampani, Z.N. Terzopoulou, D.N. Bikiaris, D.S. Achilias, D.G. Papageorgiou*, G.Z. Papageorgiou*. Exploring Next-Generation Engineering Bioplastics: Poly(alkylene furanoate)/Poly(alkylene terephthalate) (PAF/PAT) Blends, *Polymers (Q1)* **2019**, *11*, 556 (LINK)

Thank you