

Recent advances in the eco-design of sustainable copolyesters for packaging applications



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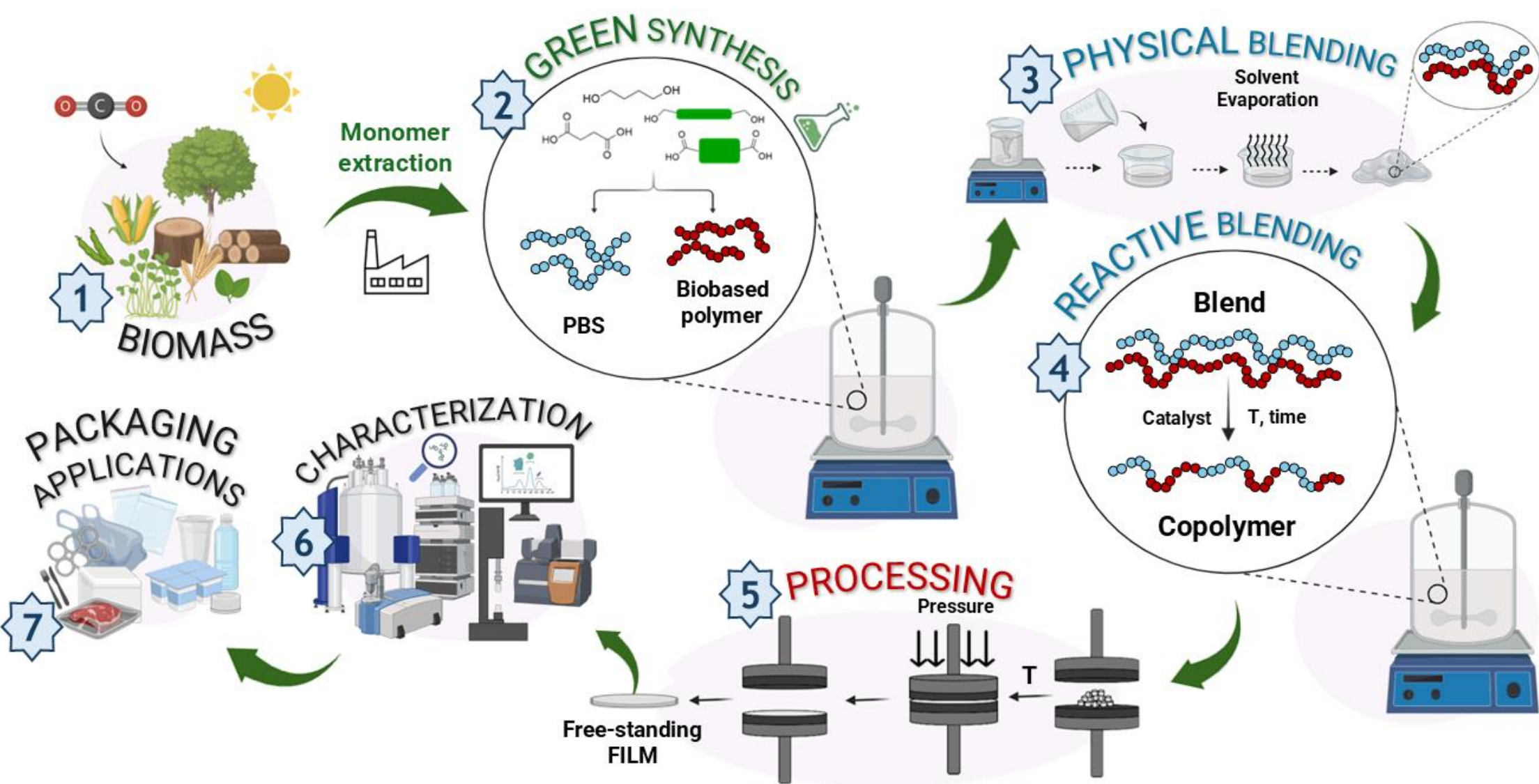
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Introduction



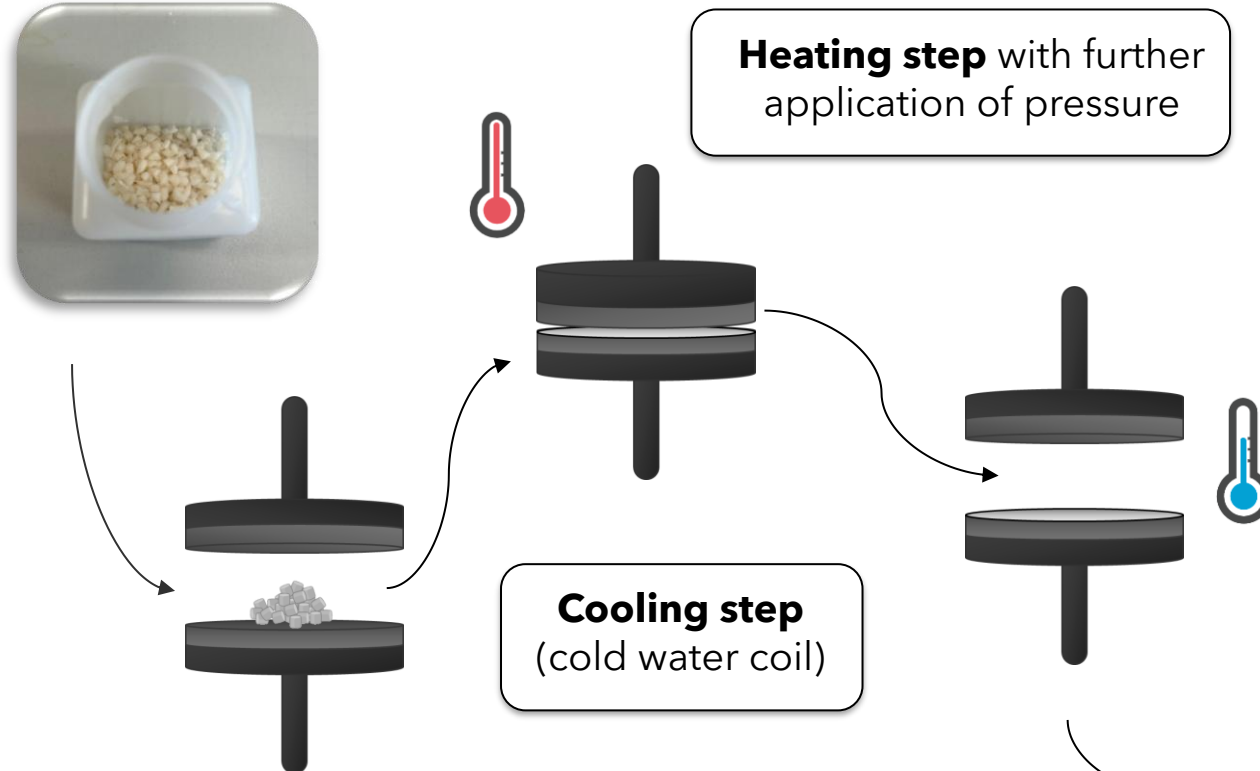
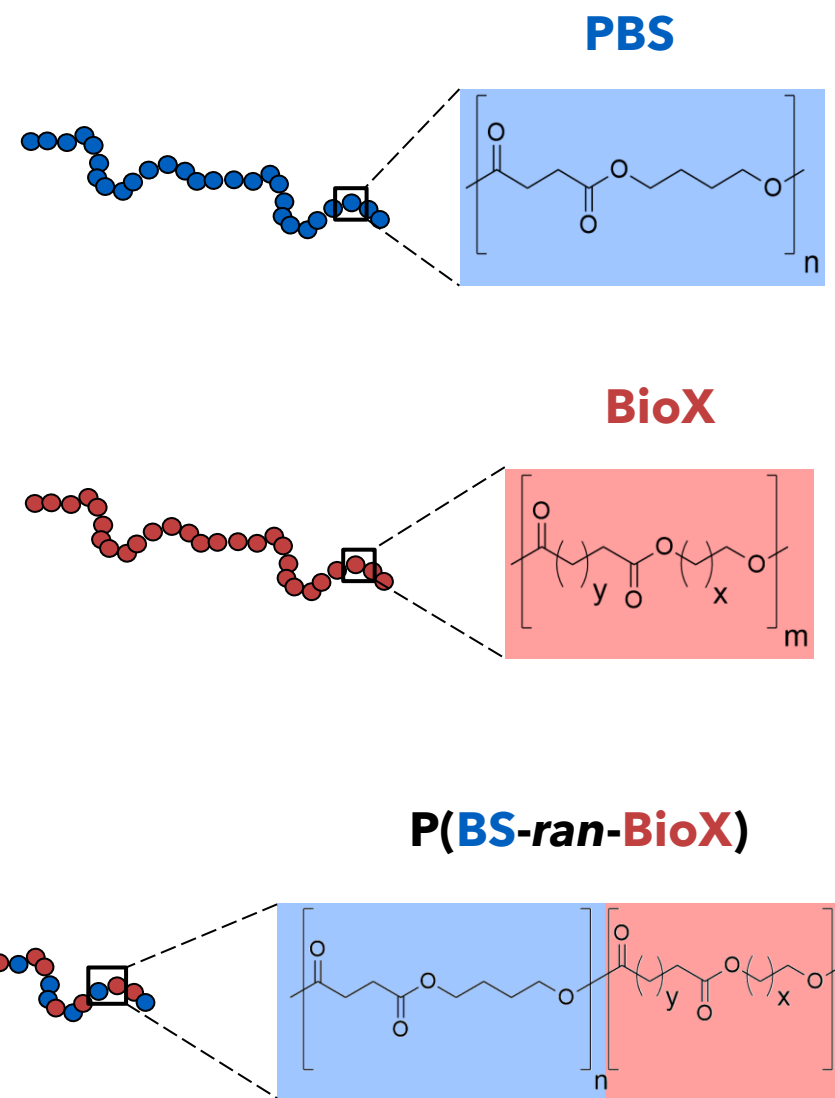
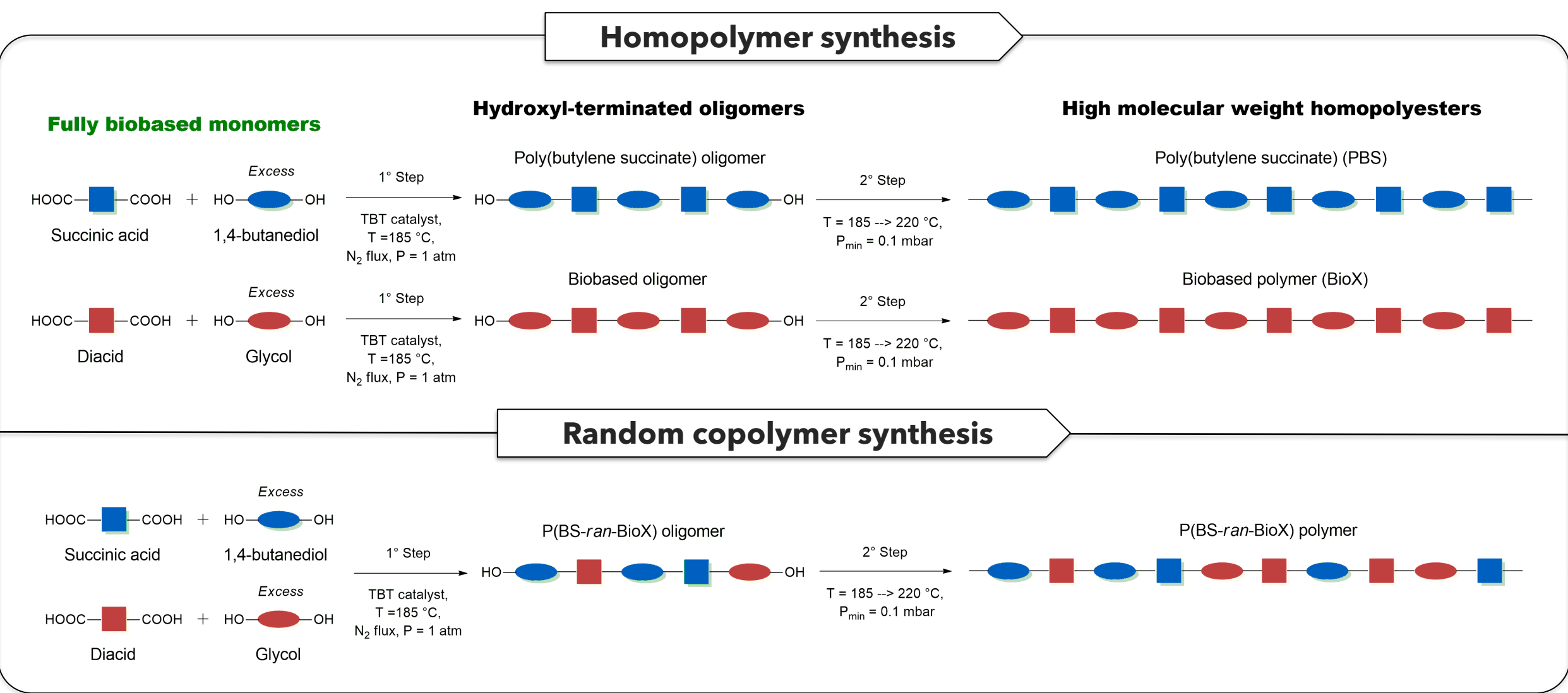
Packaging is crucial in preserving and protecting products, extending shelf life, and enhancing consumer convenience. The demand for sustainable packaging solutions has increased significantly in recent years, driven by growing concerns about environmental pollution and the high CO₂ emissions associated with plastics production and use.

Oil-based plastics are widely used in packaging due to their low cost and favorable mechanical and barrier properties. However, their negative environmental impact poses serious ecological challenges. As a result, there is a pressing need to reduce reliance on such materials by exploring alternatives with a lower carbon footprint. Among these, **bioplastics** such as **poly(butylene succinate) (PBS)** have emerged as promising sustainable options [1]. PBS is a biobased and biodegradable aliphatic polyester that offers an excellent balance of thermo-mechanical properties [2]. Yet while having these advantages, PBS is still often blended with other polymers to enhance its applicability [3].

This work presents a sustainable approach for the development of a **fully biobased alternative plastic** synthesized from poly(butylene succinate) (PBS) and another biobased polymer (BioX). The synthesis of both block and random copolymers has been carried out, as well as the achievement of different molecular architectures along with tailored property modulation. The resulting materials were processed and subjected to a complete characterization to assess their potential use as a green packaging solution.

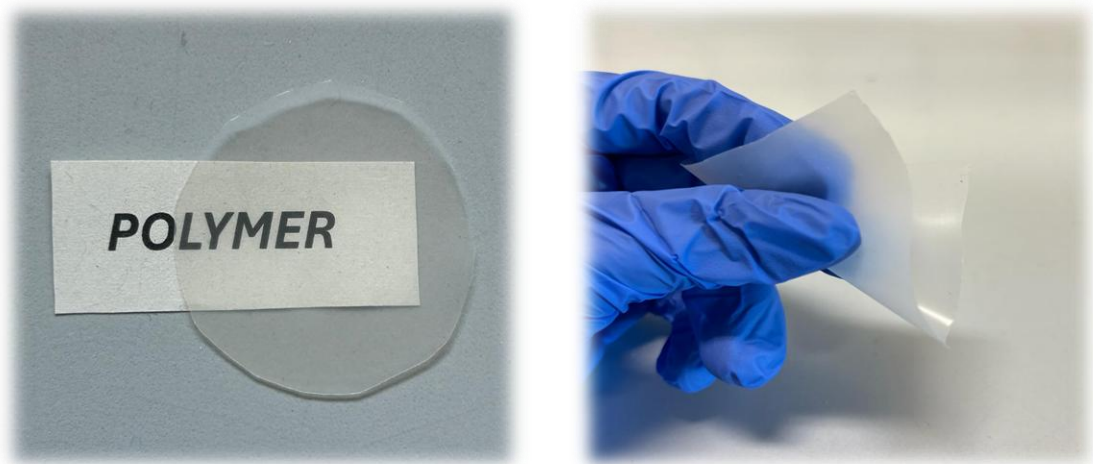
Synthetic strategy

Processing

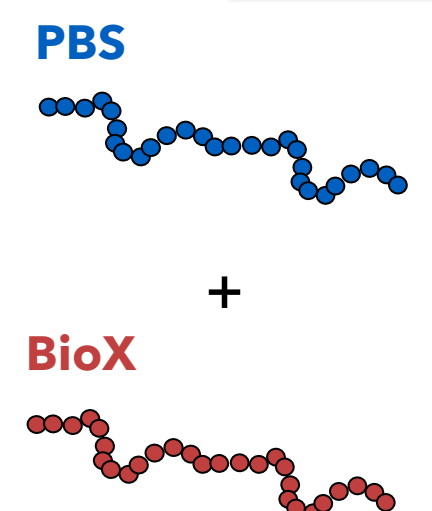


FREE-STANDING FILM
✓ High flexibility
✓ High transparency

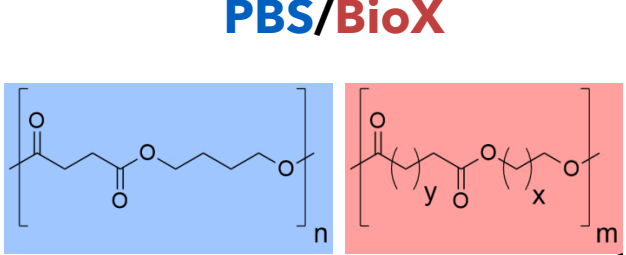
Polymer film



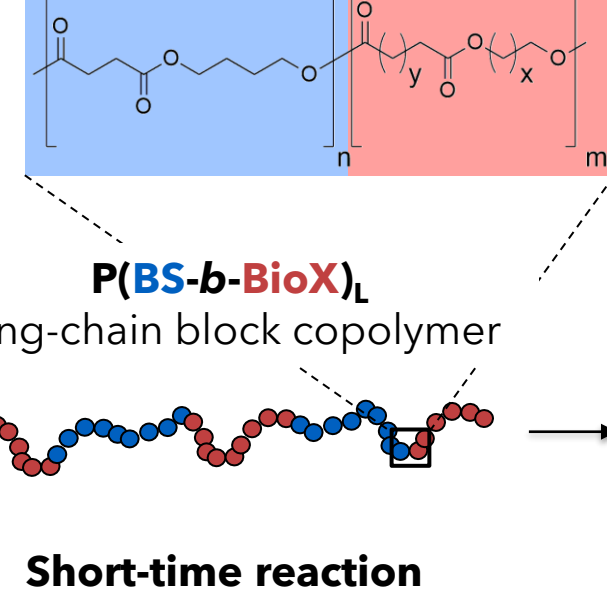
PHYSICAL BLENDING



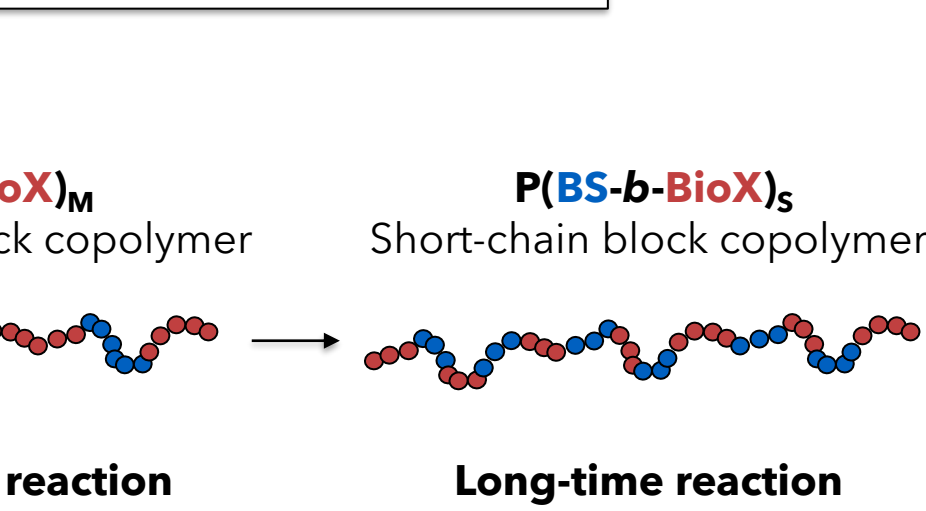
- Mixing conditions:
T = 25 °C, P = 1 atm
Common solvent
- Evaporation of the solvent and drying



P(BS-b-BioX)



REACTIVE BLENDING



Characterization & property evaluation

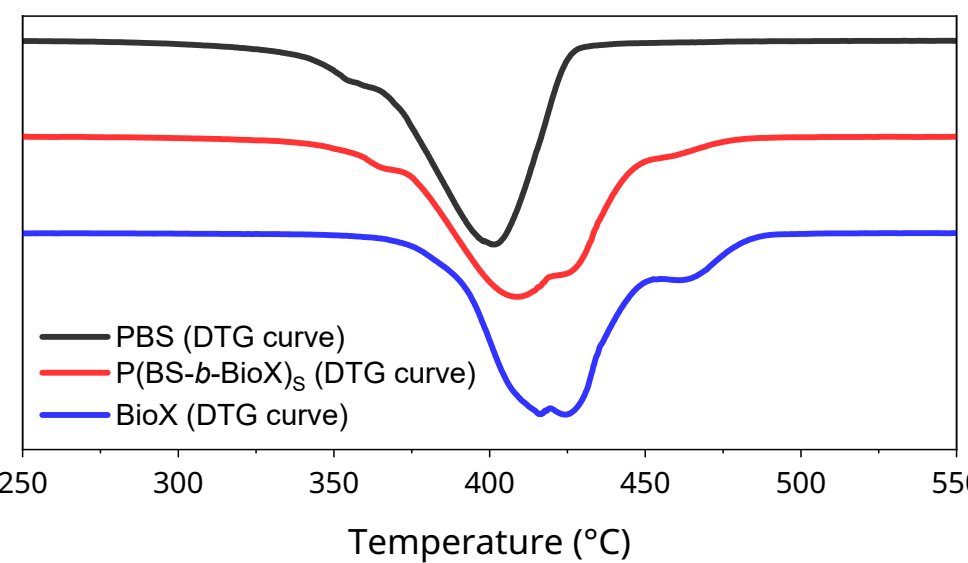
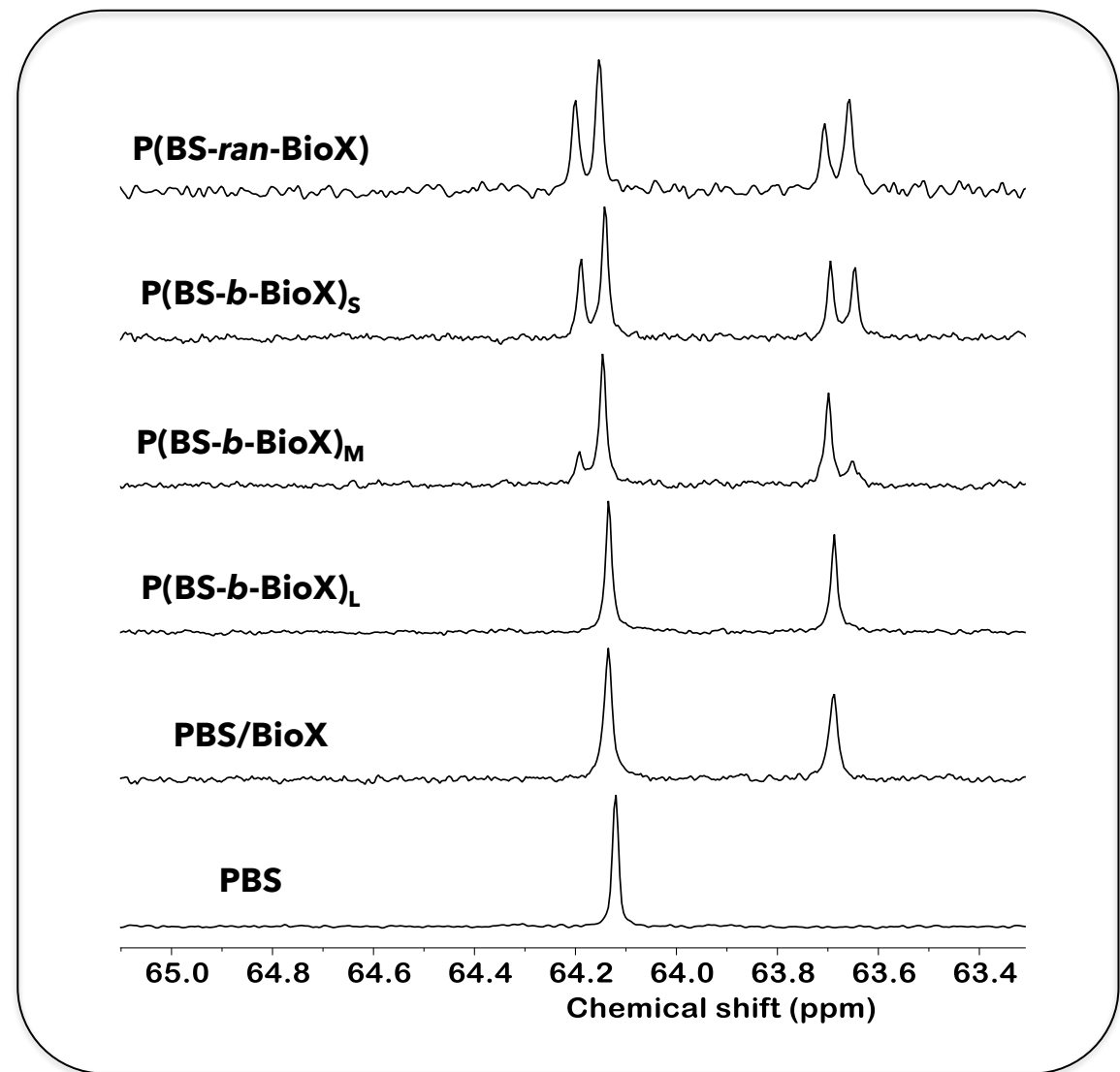
¹H-NMR, ¹³C-NMR, GPC, WCA, DSC and TGA data for homopolymers and copolymers

Polymer	PBS - wt% (feed)	PBS - wt% (¹ H-NMR)	L _{BS} ^a (¹³ C-NMR)	L _{BioX} ^b (¹³ C-NMR)	b ^c (¹³ C-NMR)	M _n - g/mol (GPC)	PDI (GPC)	θ - deg (WCA)	T _m - °C (DSC)	ΔH _m (tot) ^d - J/g (DSC)	T _{onset} - °C (TGA)	T _{max} - °C (TGA)
PBS	100	100	-	-	-	71000	1.85	86.4 ± 2.7	114	51.1	371	401
BioX	0	0	-	-	-	69000	1.95	86.1 ± 2.7	NDA	NDA	NDA	NDA
PBS/BioX	50	51	-	-	-	68000	1.96	84.7 ± 2.9	113	50.0	378	406
P(BS-b-BioX) _L	50	51	-	-	b → 0	66000	1.98	n.d.	113	47.0	378	408
P(BS-b-BioX) _M	50	51	5.3	3.9	0.45	70000	1.96	85.6 ± 2.4	93	35.4	378	408
P(BS-b-BioX) _S	50	51	2.6	1.9	0.9	78000	1.91	n.d.	72	31.5	380	409
P(BS-ran-BioX)	50	51	2.3	1.7	1.0	n.d.	n.d.	89.7 ± 2.0	67	29.5	377	405

^aBS block length; ^bBioX block length; ^cDegree of randomness; ^dTotal ΔH_m = [ΔH_m (BS) + ΔH_m (BioX)]. n.d. = not yet detected NDA = Non-Disclosure Agreement

¹³C-NMR INCREASING REACTIVE BLENDING TIME

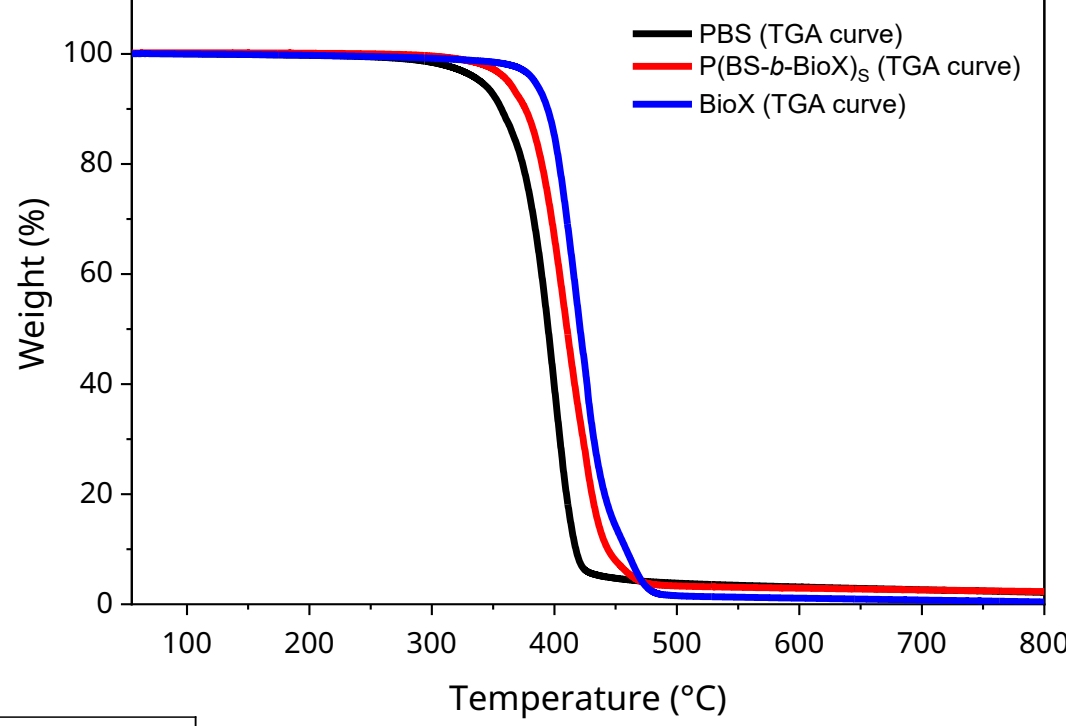
- Higher *b* → **RANDOMIZATION**
- Reduction in the length of the blocks → **TRANSESTERIFICATION**
- Degree of randomness equal to 1.0 for the random copolymer obtained from the monomers.



DSC

Effect of copolymerization on thermal behaviour

- T_m modulation observed across the entire copolymer series and in the random copolymer.
- Decrease in ΔH_m along the series indicates reduced crystallization capability.



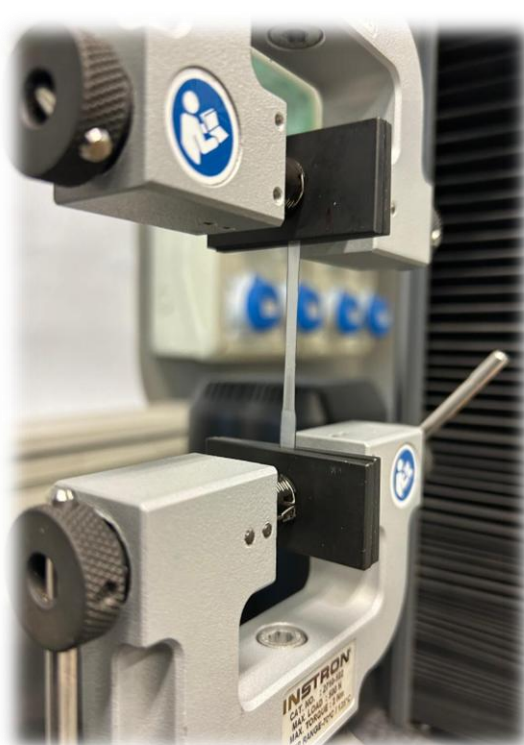
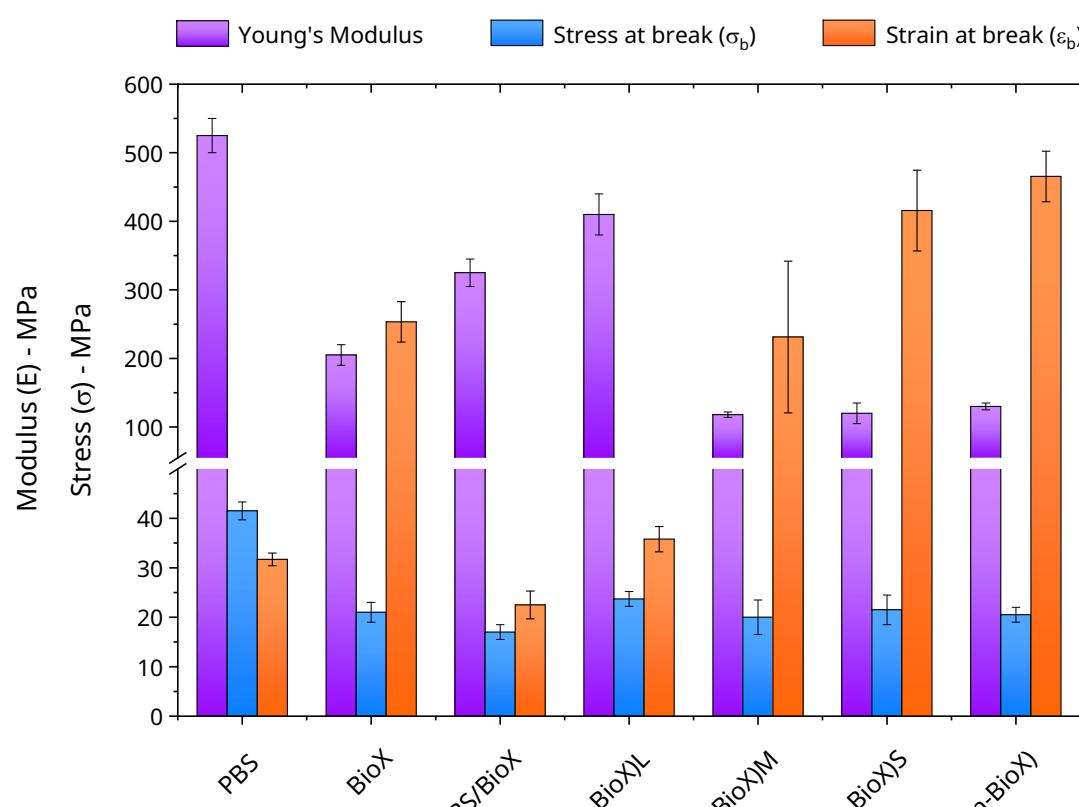
TGA

- Higher thermal stability:
 - T_{onset} > 375 °C
 - T_{max} > 405 °C
- Easy processability

Tensile test

FLEXIBILIZATION OF PBS

- Decrease in Young's Modulus (E) along the copolymer series:** Approximately 70% of reduction observed, remaining stable from *b* = 0.45 to *b* = 1.0.
- Increased elongation at break (ε_b) and decreased stress at break (σ_b):** These changes occur while maintaining high toughness throughout the entire copolymer series.
- Mechanical properties optimized and suitable for **FLEXIBLE PACKAGING APPLICATIONS**.



Conclusions

Key Results

- Bio-derived feedstocks and green synthetic methods minimize environmental impact, enhancing overall process sustainability.
- Copolymerization enables tailored improvements of PBS thermo-mechanical properties - **enhanced flexibility, higher thermal stability and transparency**.
- Copolymers demonstrate strong suitability for sustainable flexible packaging applications.

Future Developments

- Evaluation of the reactive blending process scalability toward industrial implementation.
- Characterization of gas-barrier properties, including O₂ and CO₂ permeability measurements.
- Investigation of biodegradability in different environments, including compostability assessments.

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References

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- Gigli, M. et al. *Polym. Chem.* **2016**, *75*, 431-460.
- Barletta, M. et al. *Prog. Polym. Sci. Chem.* **2022**, *132*, 101579.