DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

UNIVERSITÀ DEGLI STUDI DI PADOVA

Polymer Engineering Group

ANPE

The glycolysis process of polyamide 6

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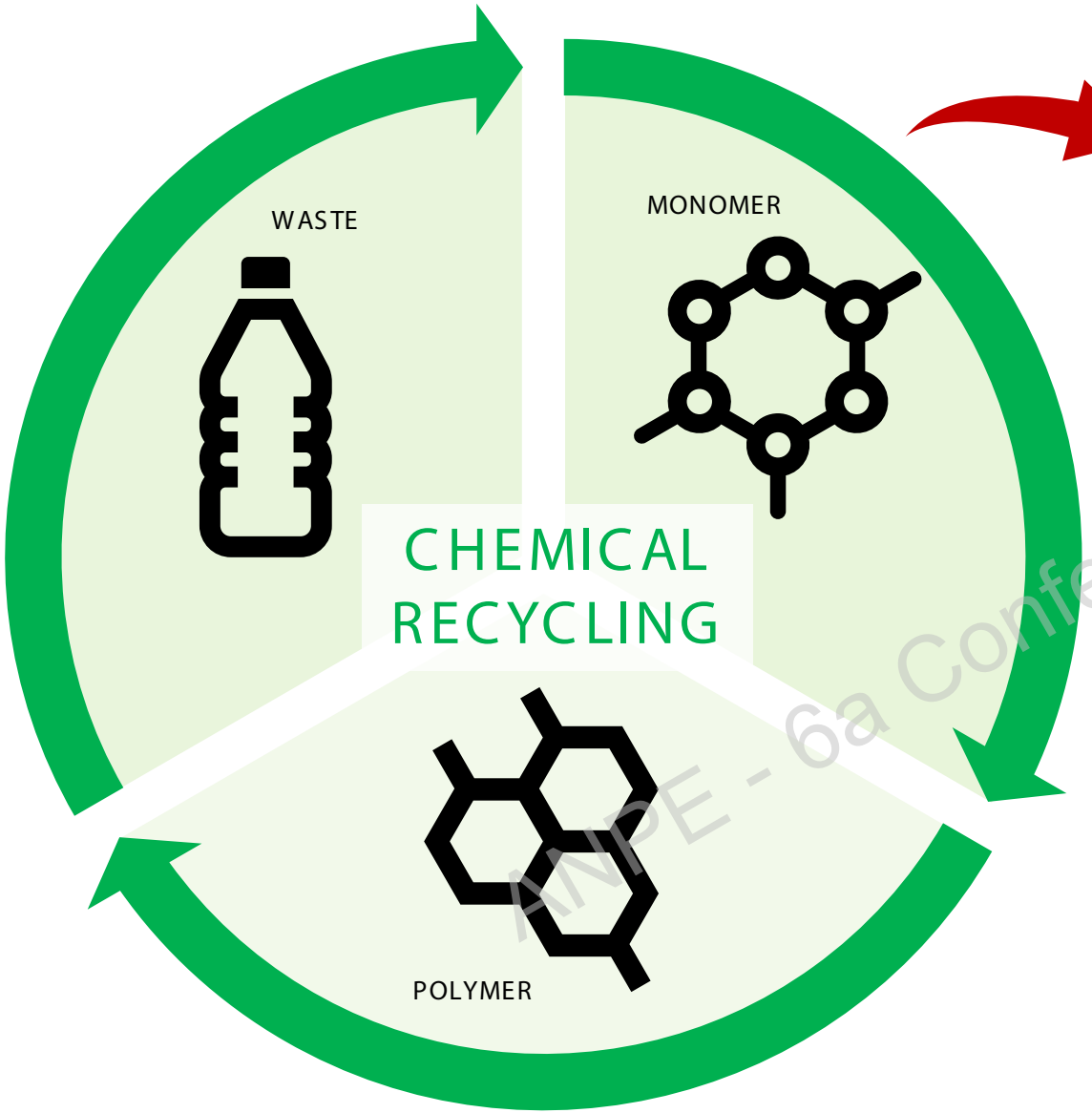
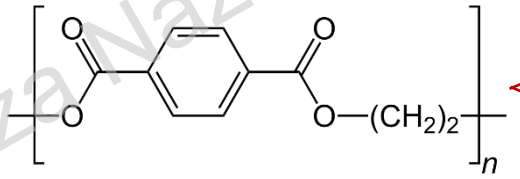
6ª Conferenza Nazionale Poliuretano Espanso Rigido
30 may 2024



Glycolysis process

Viable recycling strategy for:

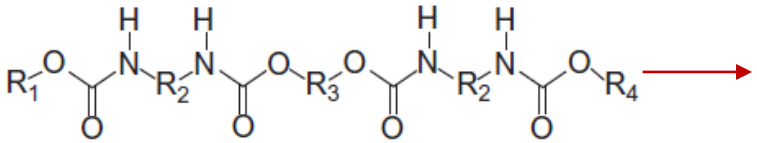
PET



BHET (monomer)

Polyester polyols

Polyurethane (PU)

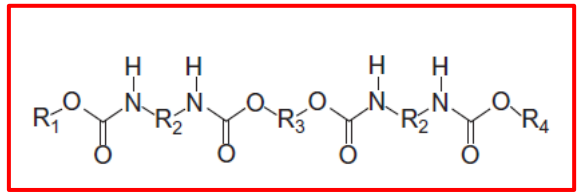


Polyester polyols

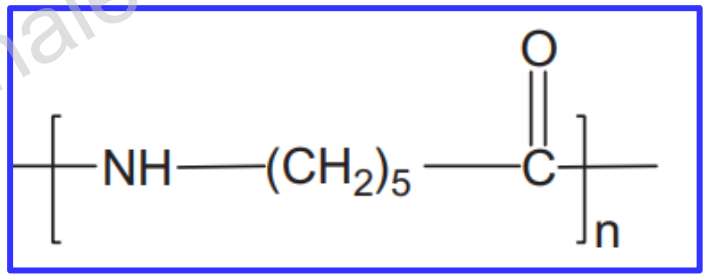
Applicability to nylon 6 ?

Material covered by the study

Flexible polyurethane (PUFs)



MAIN FOCUS



Polyamide 6 (PA6) fabric

Theme developed in two sequential master thesis

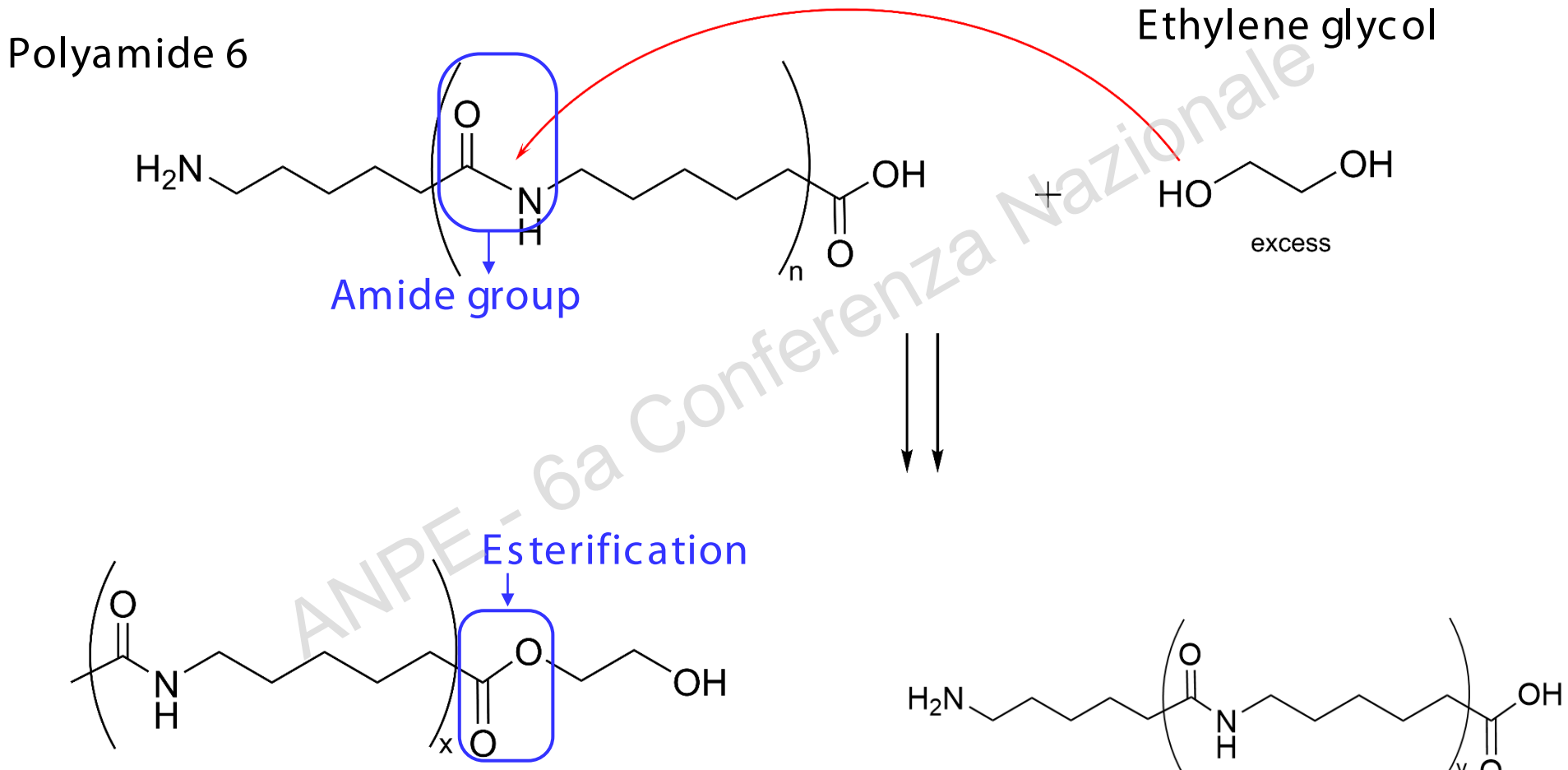
APPROACH 1

Conventional and microwave PA6 glycolysis (acid catalysis)

APPROACH 2

Polyamide 6 glycolysis and acidolysis (basic catalysis)

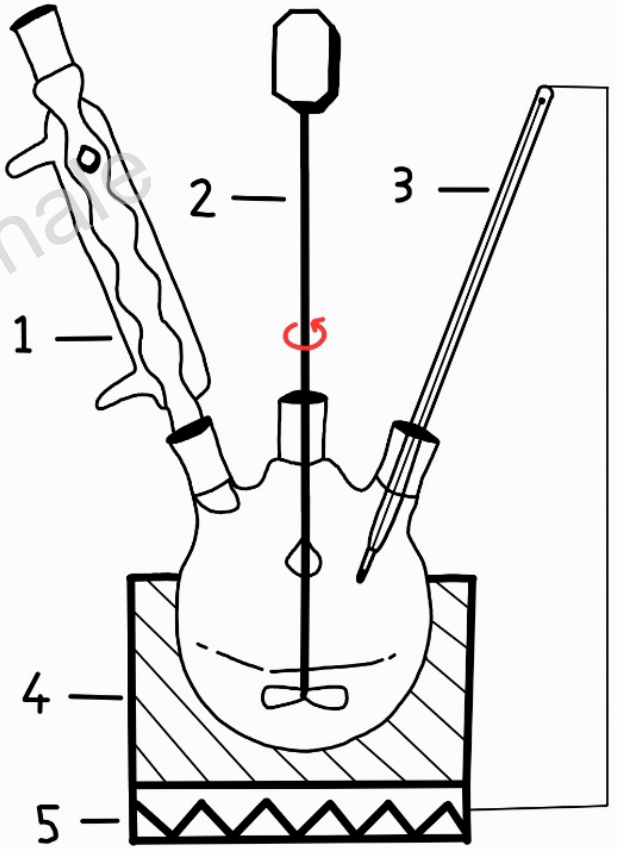
Polyamide 6 glycolysis reaction



Glycolysis using conventional heating

Operating parameters

- Glycol-polymer ratio
- Type and content of catalytic system
  (DAP = hydrogen diammonium phosphate)
- Reaction temperature
- Reaction time



Various experimental tests were performed, using different settings

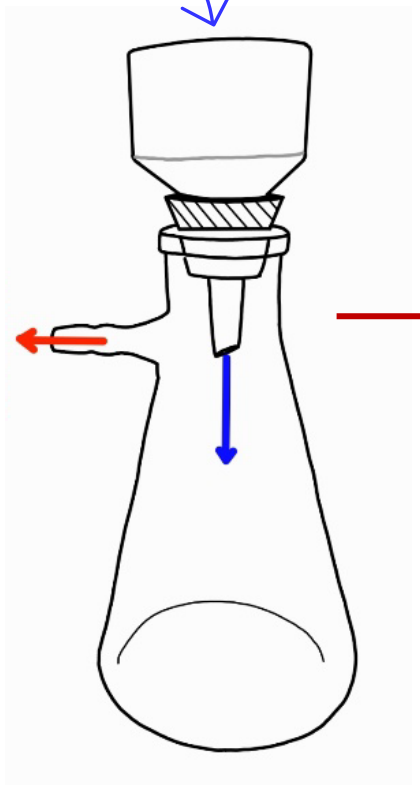
	Polymer [g]	Glycol	Glycol: polymer ratio	Catalyst	[mmol/100g]	T [°C]	Reaction time [h]
G40	100	MEG	3:1	DAP	220	190	27

Main glycolysis test of nylon 6 performed with conventional heating

Long reaction time
Acid catalysis with DAP
Excess of MEG

Characterization techniques of the samples

Sample



WASHING

Filtration liquids

HPLC-MS

Washed with ethanol

GC-MS

Washed with hot water

Solid residue

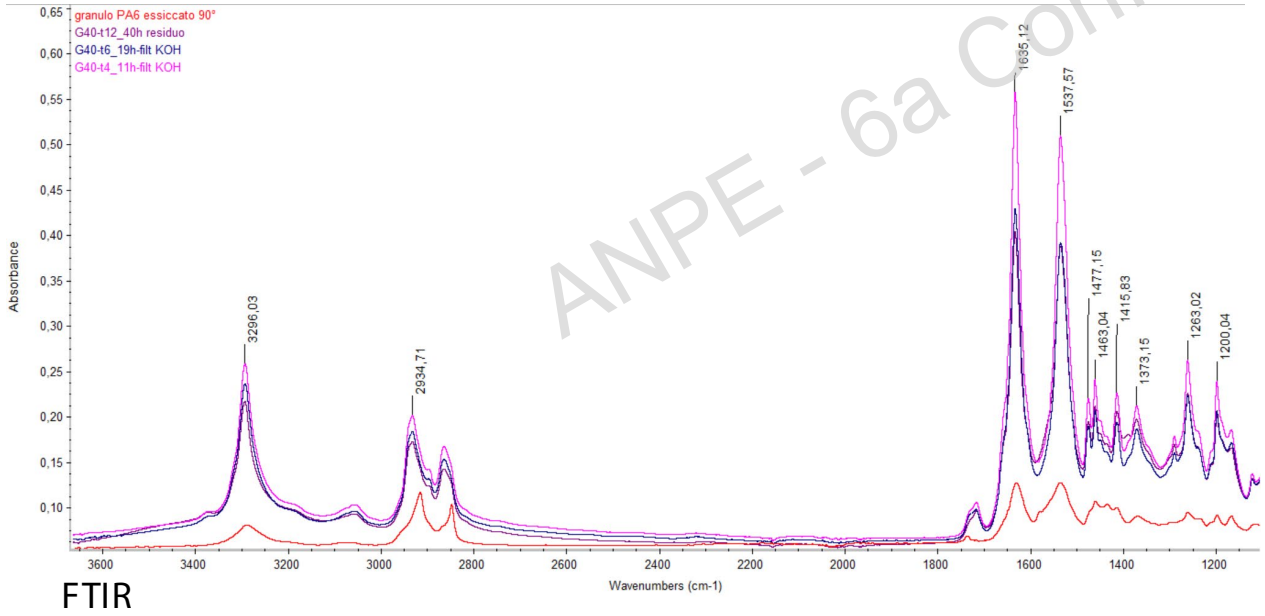
DSC

FTIR

Analysis of the solid residue

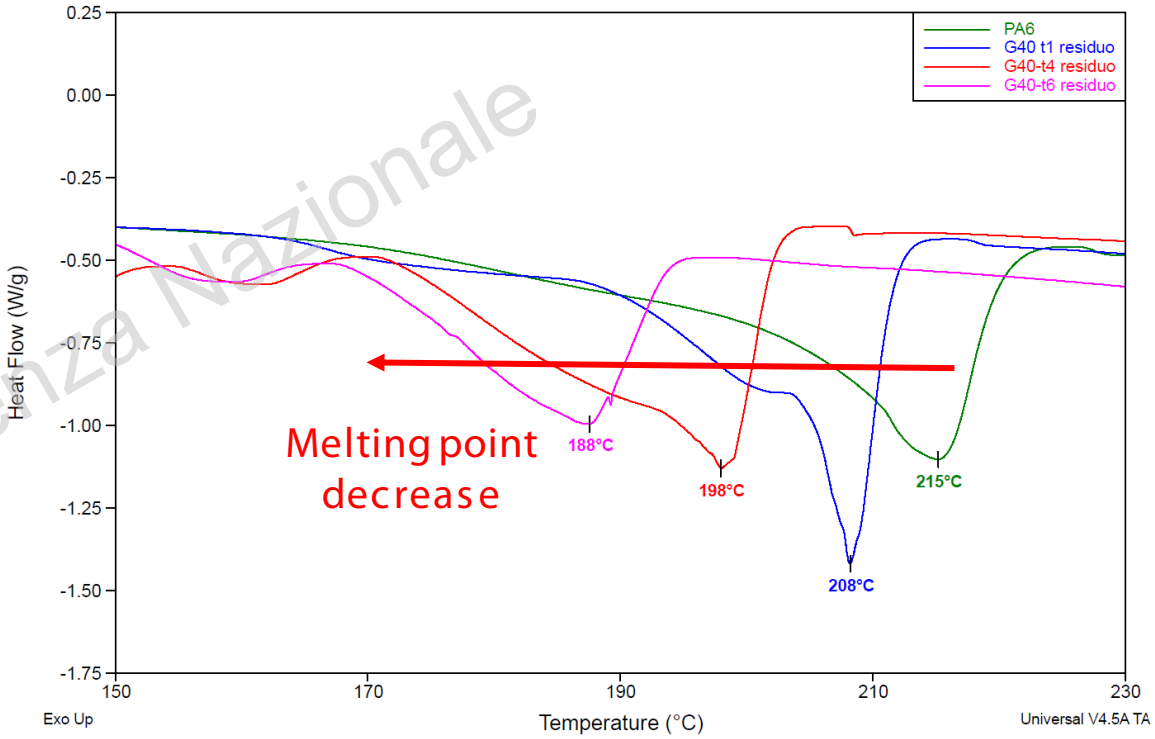
Progressive reduction of the collected solid residue

Sample	Residue mass [g]	Estimated yield η [%]
5h	1,5	20
11 h	0,8	50
19 h	0,2	80
27 h	less than 0,05	99



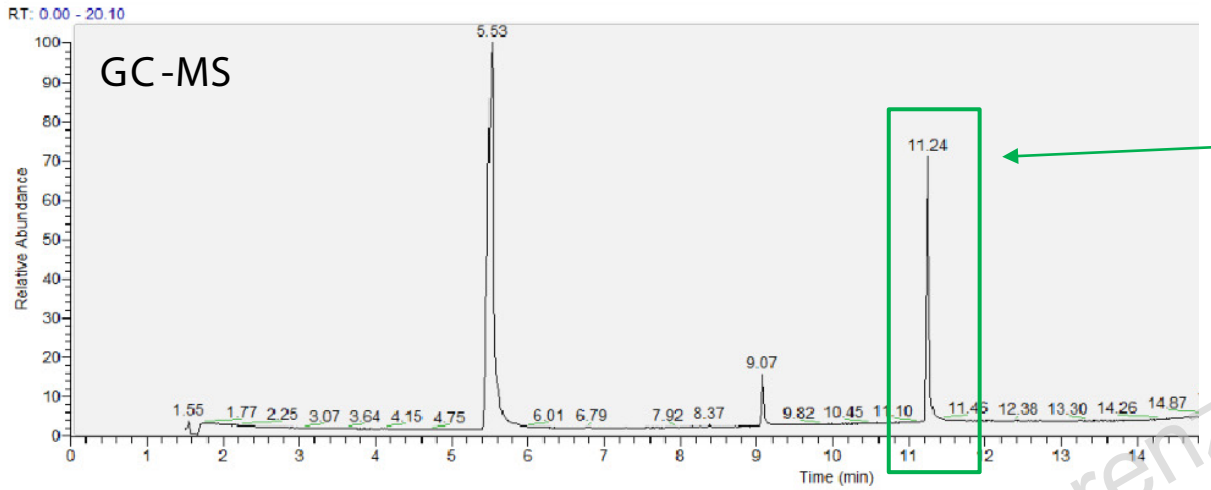
FTIR

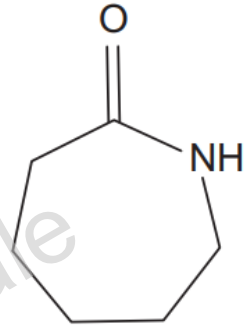
DSC



The remaining solid fraction was the depolymerization residue

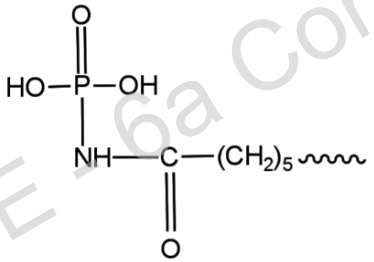
Characterization of liquids and polyols

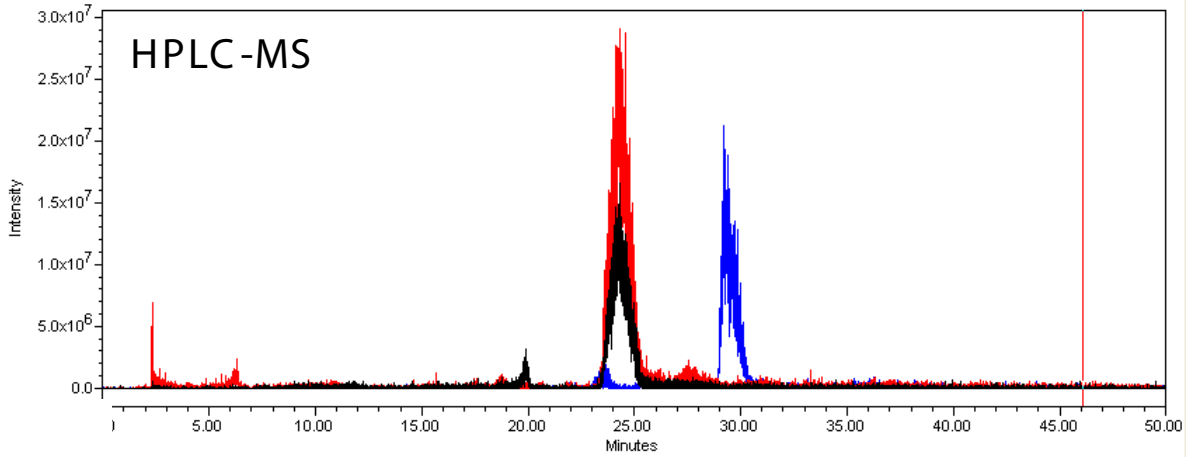




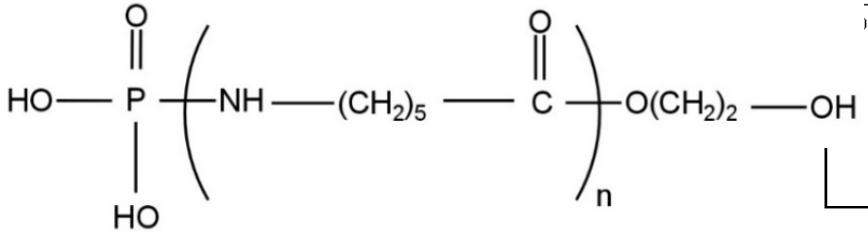
ε-Caprolactam (114 m/z)
Monomer of polyamide 6

Oligomers of polyamide 6
with phosphorous end groups
(253 m/z)





Polyester polyols
with phosphorous
end groups
(298 and 410 m/z)



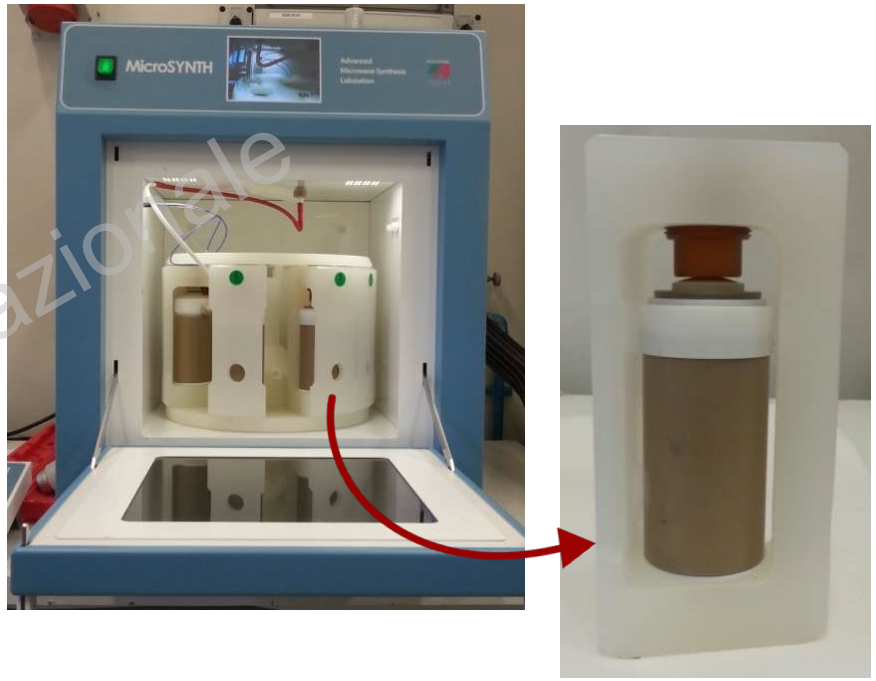
Products of polyamide 6 glycolysis

Microwaves-aided glycolysis of PA6

Conventional heating required very long reaction times

OPERATIONS WITH MICROWAVE REACTORS

- Fast heating
- Abatement of the reaction time
- Working under pressure



	Polymer [g]	Glycol	Glycol: polymer ratio	Catalyst	mmol/100g	T [°C]	Power [W]	Reaction time [min]
G43	21	MEG	3:1	Phosphoric acid 85%	220	250	400	30

Results:

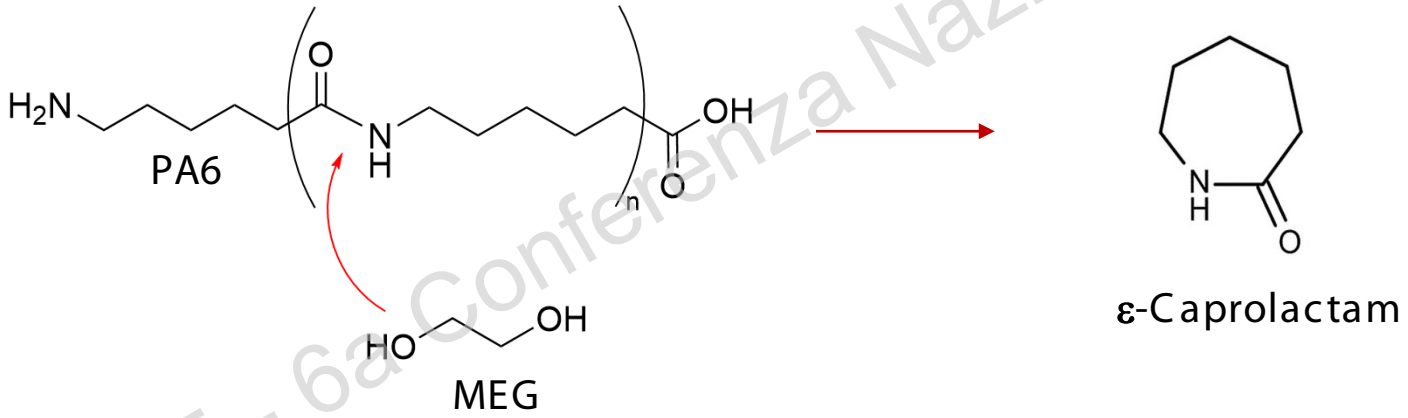
- Absence of solid residue after 30 min;
- Formation of the same compound obtained with conventional heating.

Approach 2:

PA6 glycolysis with BASIC CATALYSTS

1° PHASE:

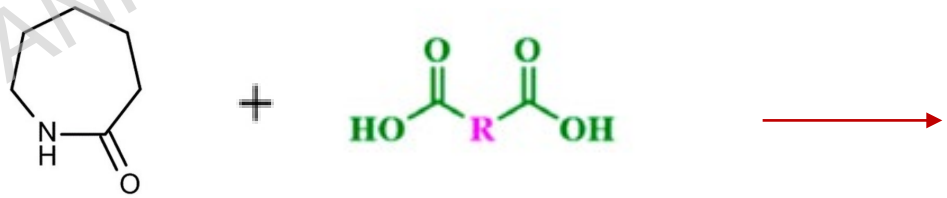
PA6 GLYCOLYSIS
and
ε-CAPROLACTAM
FORMATION



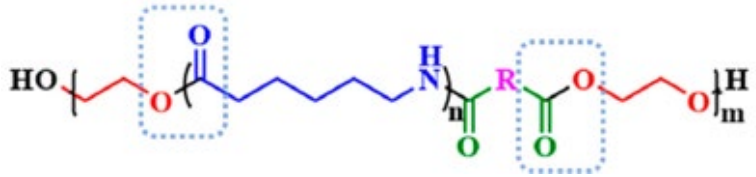
ε-Caprolactam

2° PHASE:

ε-CAPROLACTAM
REACTION



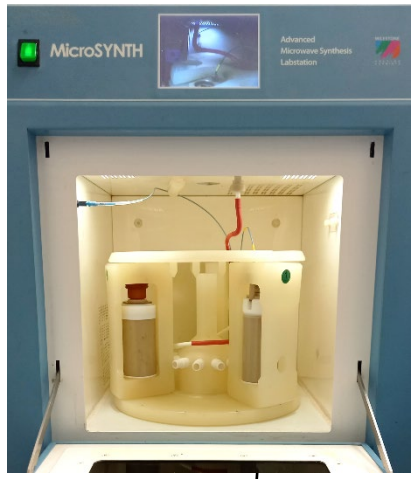
ε-Caprolactam Dicarboxylic acid

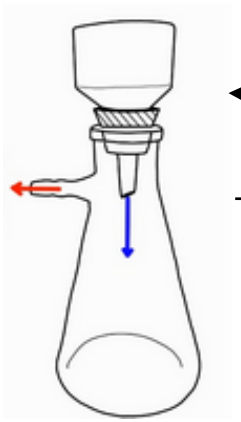


Recycled polyols

1° PHASE: PA6 GLYCOLYSIS AND ε-CPL FORMATION

Microwave heating





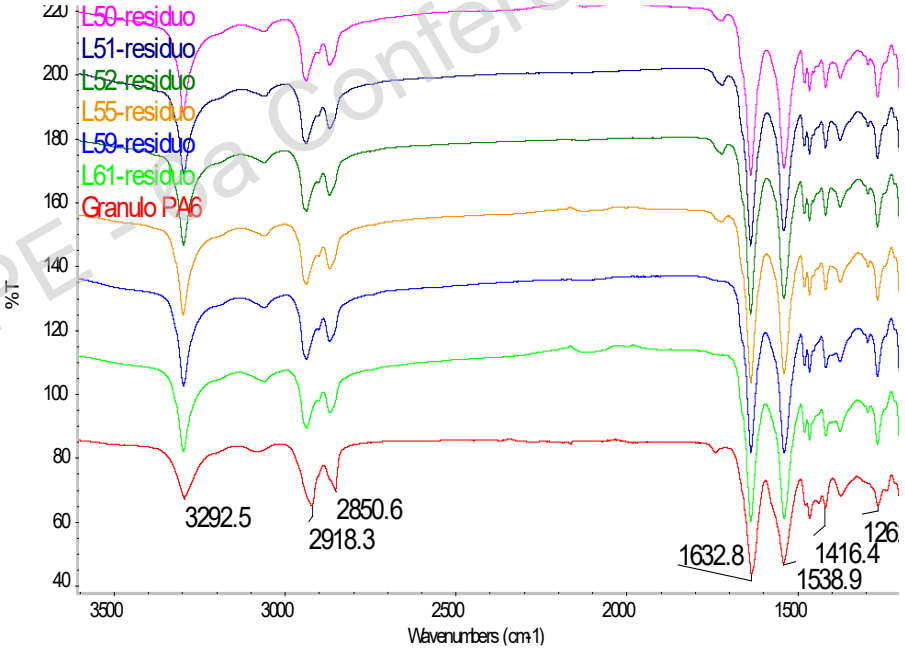
SOLID RESIDUE

Filtration

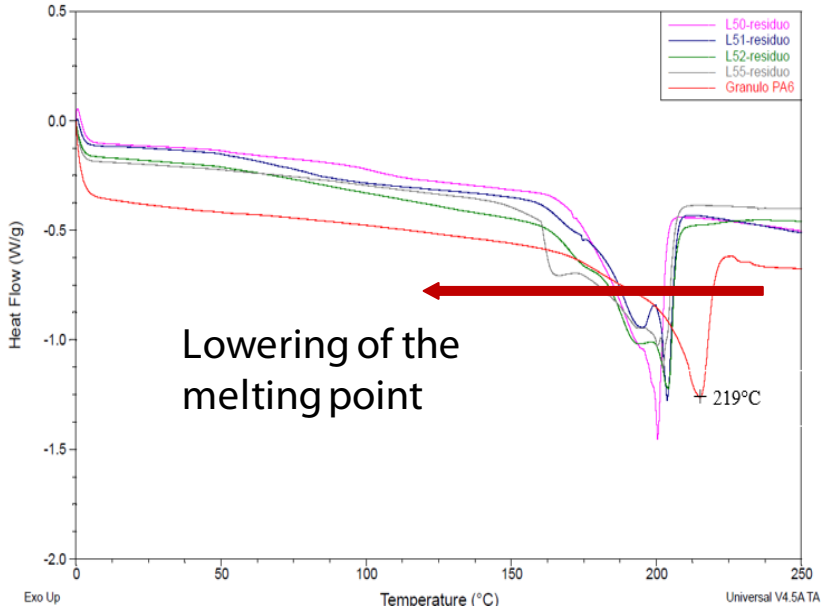
OPERATING PARAMETERS

- Catalyst (NaOH, TBT, TiP, NaOGli)
- Content of catalytic system
- Glycol-polymer ratio (3:1, 2:1, 1:1)

FTIR : residue = PA6



DSC : Depolymerization PA6



1° PHASE: PA6 GLYCOLYSIS AND ε-CPL FORMATION

Material	Polymer [g]	MEG [g]	Glycol: polymer ratio	Catalyst [mmol]	T [°C]	Reaction time [min]
PA6	7	21	3:1	52	250	30

Best catalytic system:
NaOH

Microwave heating at 250°C:

Glycolyzate obtained

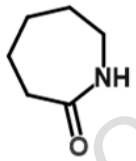
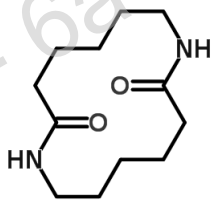
- Content of NaOH
- Glycol-polymer ratio

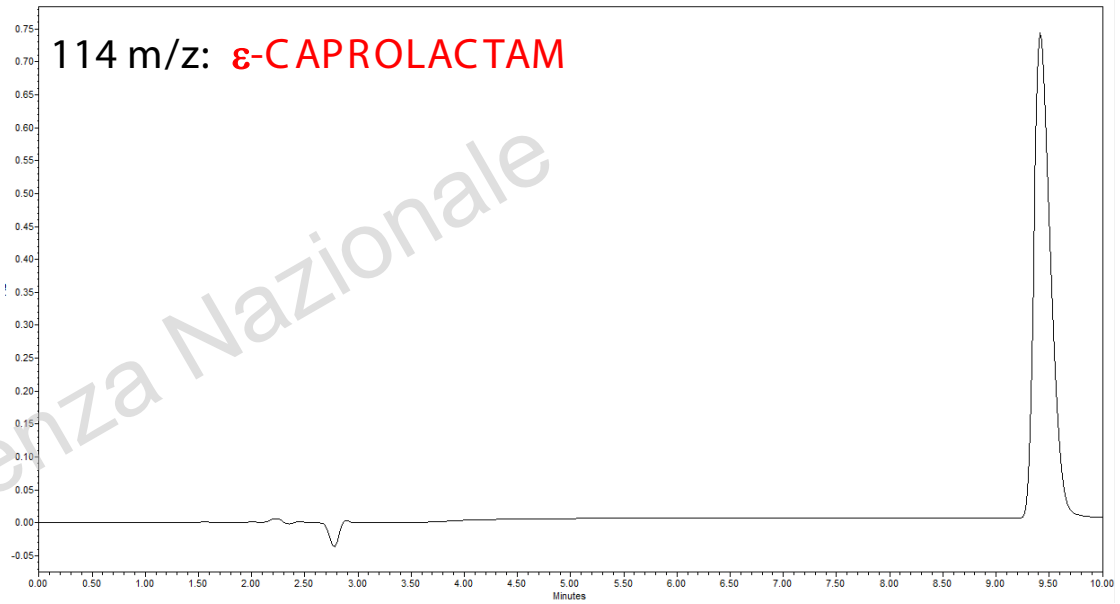
	NaOH [mmol]	Glycol:polymer ratio	T [°C]	Reaction time [min]	Solid residue [%]
L53	52	3:1	250	30	0 (<1)
L47	18	3:1	250	30	0 (<1)
L55	5	3:1	250	30	15
L59	18	2:1	250	30	4
L61	18	1:1	250	30	11

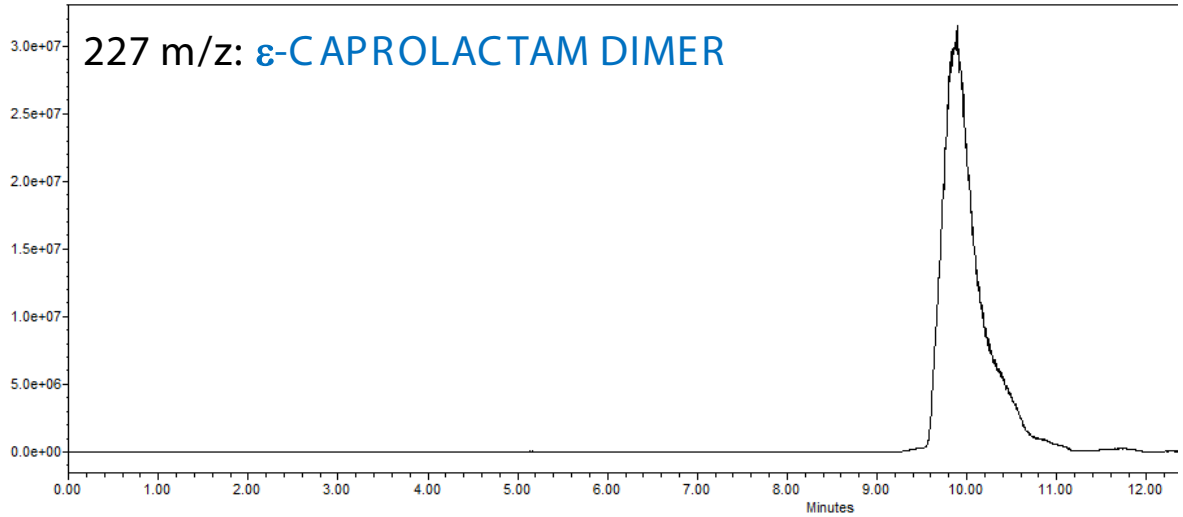
1° PHASE: PA6 GLYCOLYSIS AND ε-CPL FORMATION

Approach 2

Composition analysis (HPLC-MS):

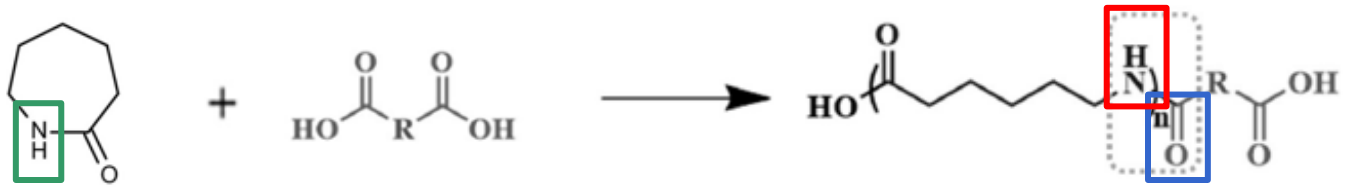
Species	Ion	Fragment	Structure
ε-caprolactam	$(M+H^+)$	113 + 1 = 114 m/z	
ε-caprolactam dimer	$(M+M+H^+)$	113 + 113 + 1 = 227 m/z	

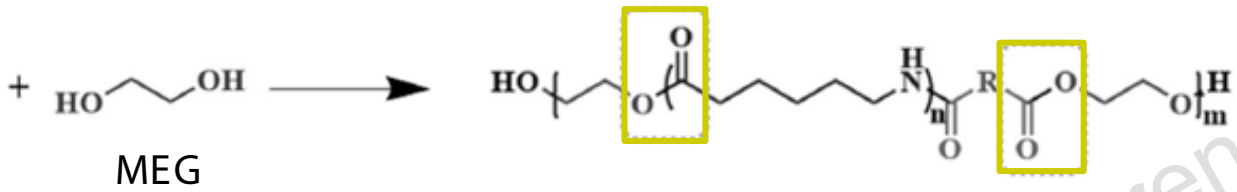




2° PHASE: ε-CAPROLACTAM REACTION

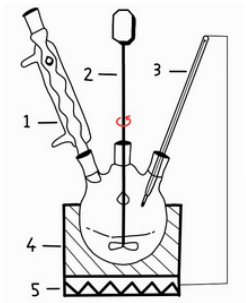
Approach 2





Reaction conditions:

- 190°C
- 13 h
- NaOH as catalyst



Model reaction reagents:

3 reagents
ε-CAPROLACTAM (CPL)
MEG
SEBACIC ACID

4 characteristic peaks

Wavenumber [cm^{-1}]	Bond	Functional group
~1736	>C=O	Carbonyl group of the ester of acid+MEG or CPL+MEG
~1625-1650	>C=O	Carbonyl group of CPL and acid+CPL
~1560	$-NH_2$	Amide I from CPL opening
~1550	>NH	Amide II in the bond of acid+CPL

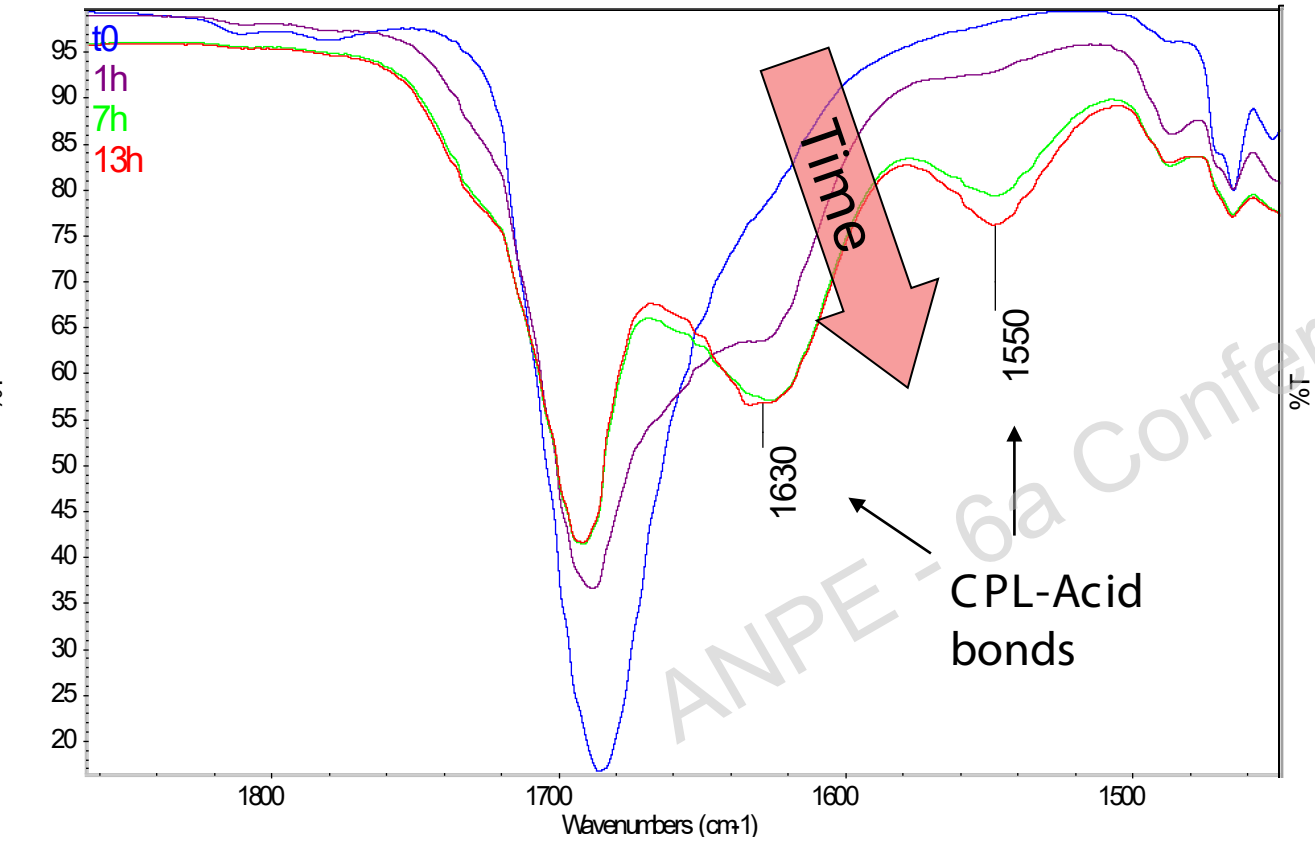
Zhang, S. et al. A novel synthetic strategy for preparing polyamide 6 (PA6)-Based polymer with transesterification.

2° PHASE: ε-CAPROLACTAM REACTION

Approach 2

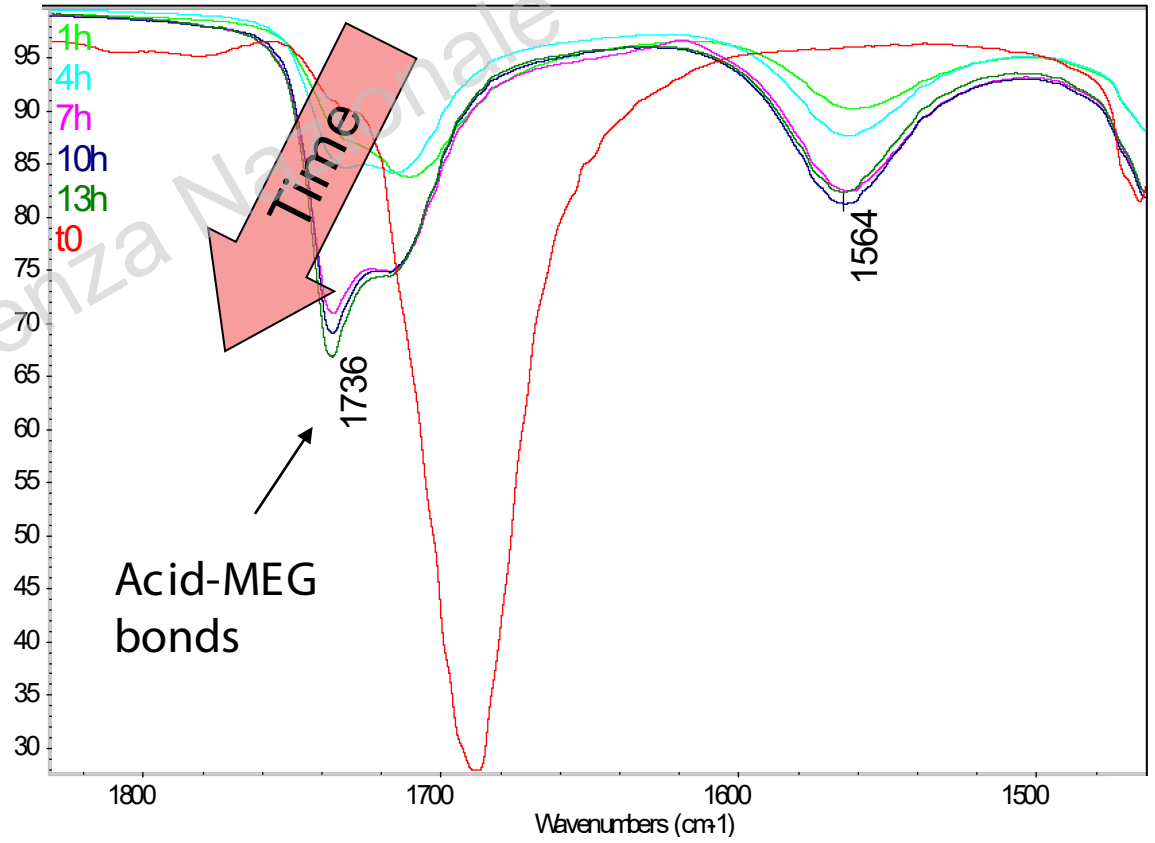
FTIR analysis of the model reactions:

Reaction: CPL + SEBACIC ACID



CPL + ACID = The reaction intermediate was formed with and without NaOH

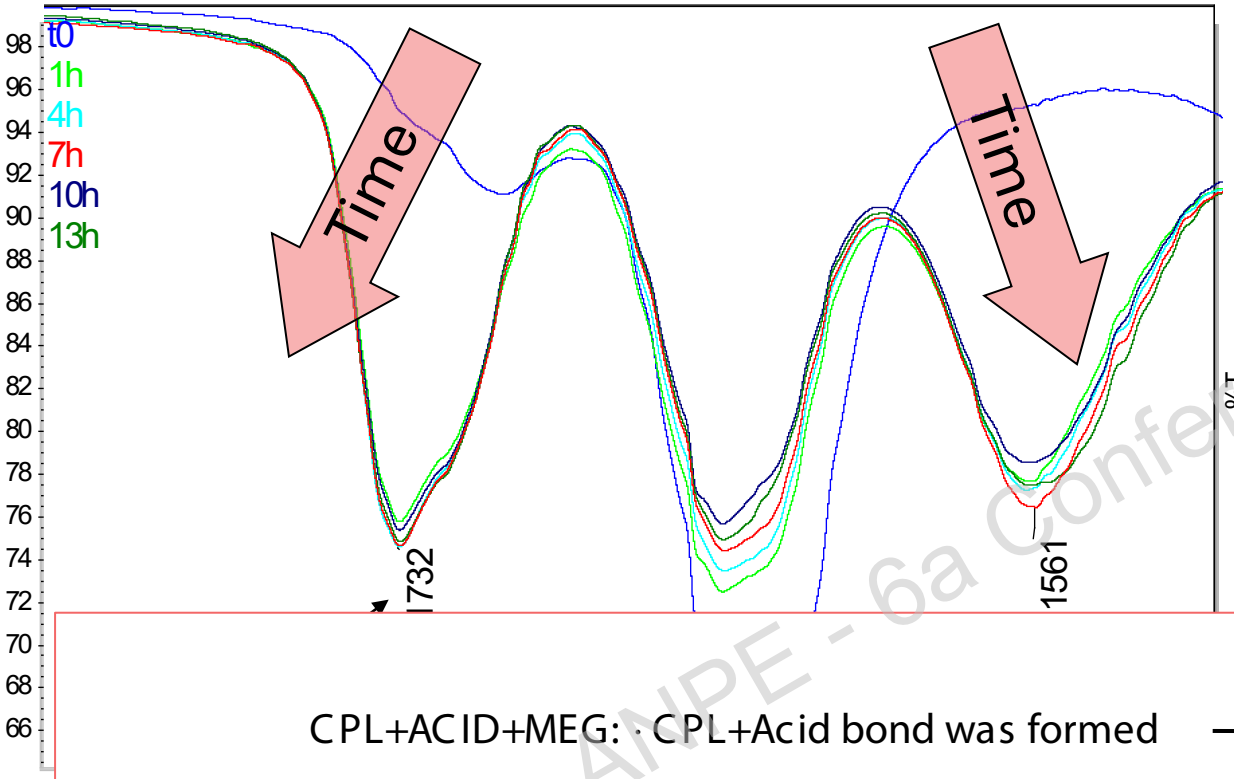
Reaction: MEG + SEBACIC ACID + NaOH



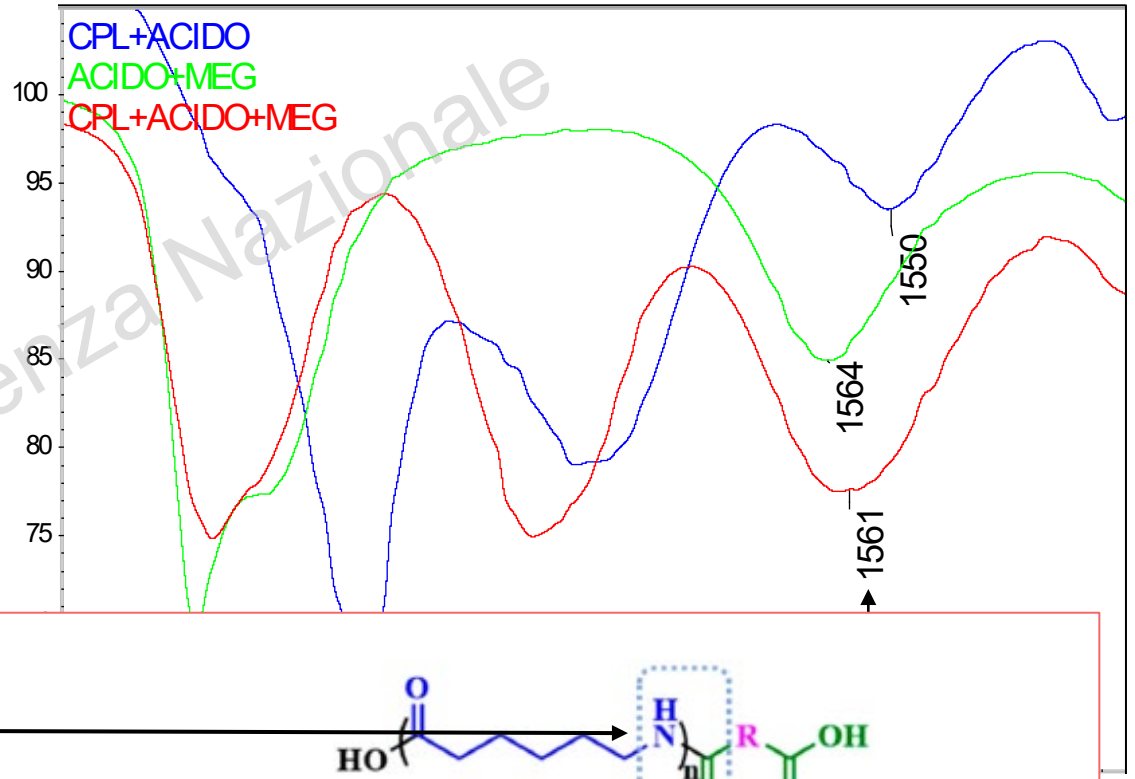
MEG + ACID = ester group was formed

2° PHASE: ε-CAPROLACTAM REACTION

Reaction: CPL + SEBACIC ACID + MEG



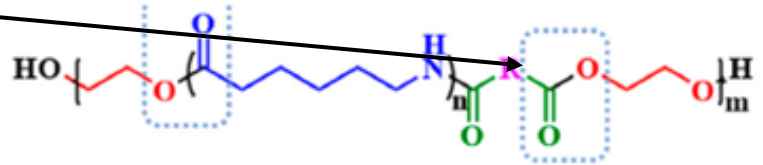
Comparison of reactions at the same time



CPL+ACID+MEG: · CPL+Acid bond was formed

Reaction intermediate

· Bond between the reaction intermediate and MEG was formed



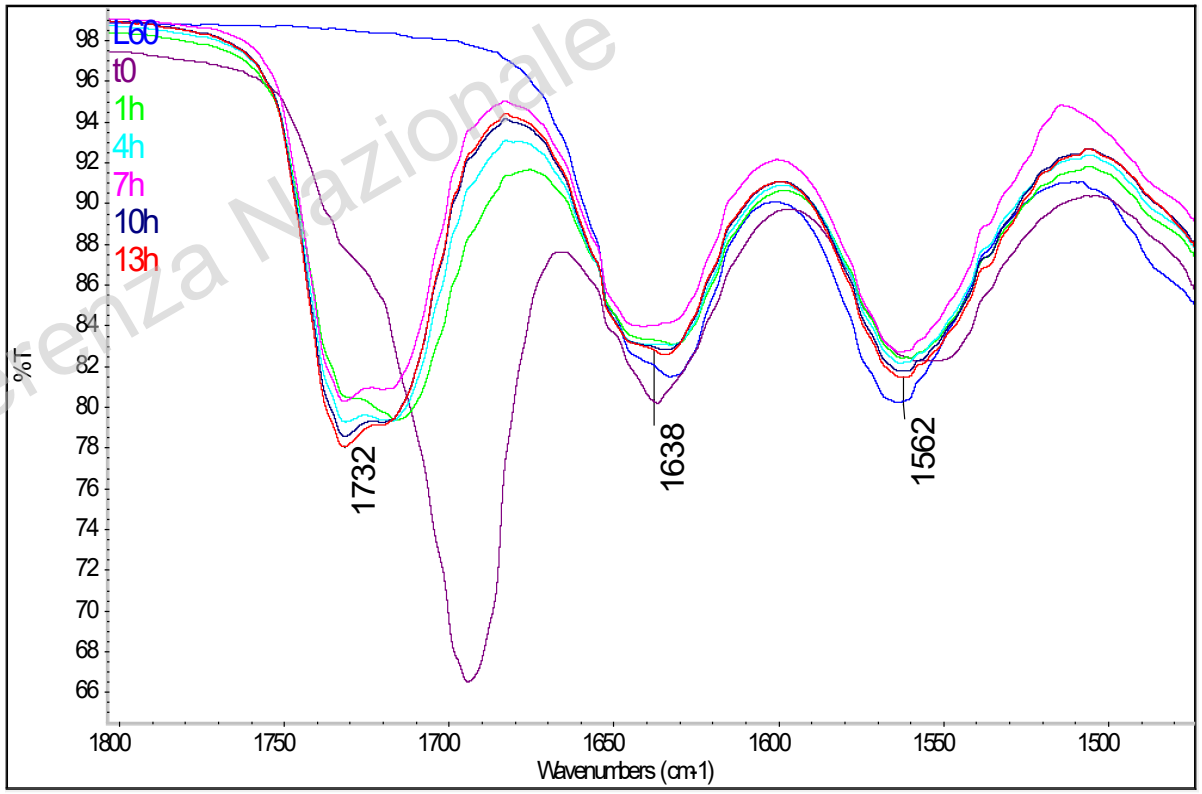
Recycled polyol

2° PHASE: ε-CAPROLACTAM REACTION

Reactions between glycolyzate and sebacic acid:

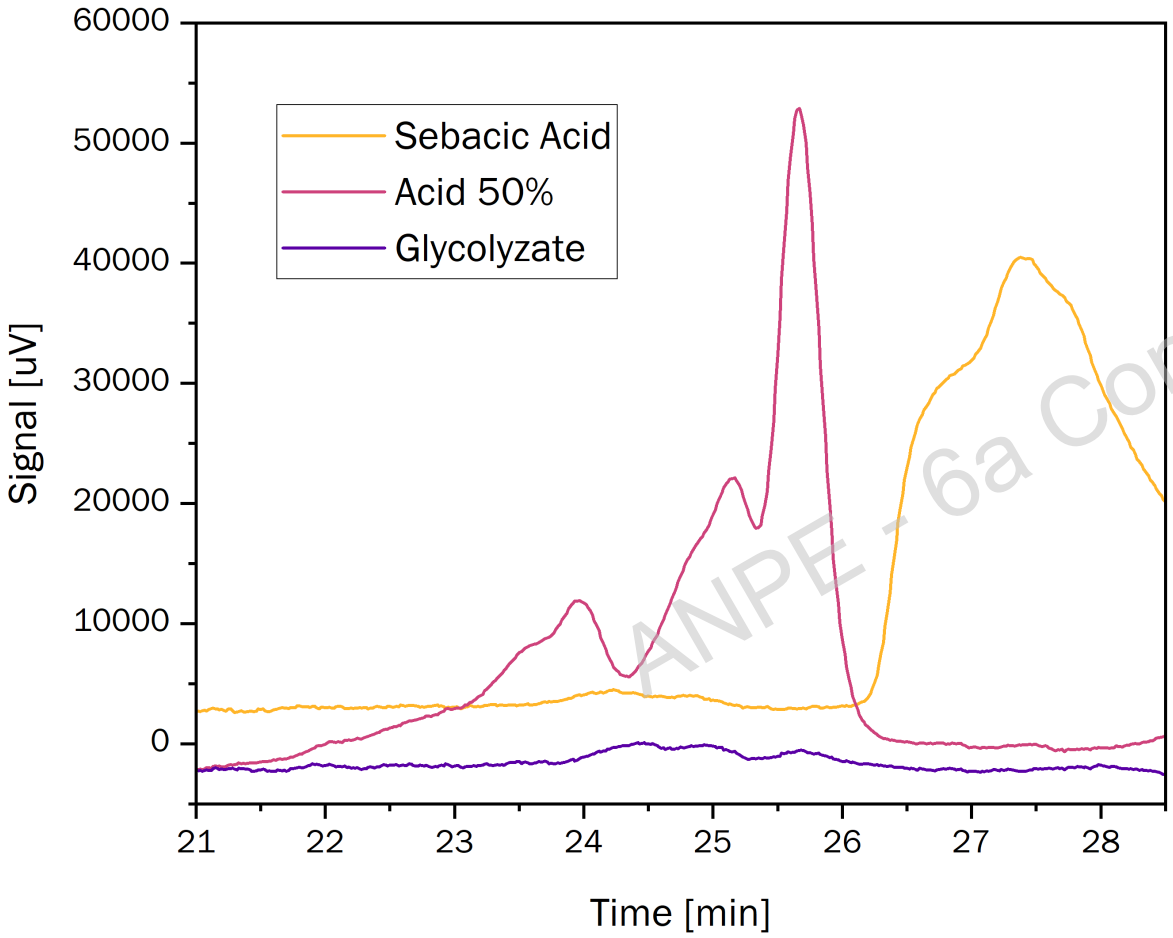
Operating parameters	Percentage of sebacic acid relative to the moles of CPL present : 100%, 50% and 10%.

	Glycolyzate [g]	CPL [mmol]	Sebacic acid [mmol]	Sebacic acid [g]	T [°C]	Time [h]
ACID 100%	24.0	53	53	10.73	190	13
ACID 50%	24.0	53	26	5.36	190	13
ACID 10%	24.0	53	5.3	1.07	190	13

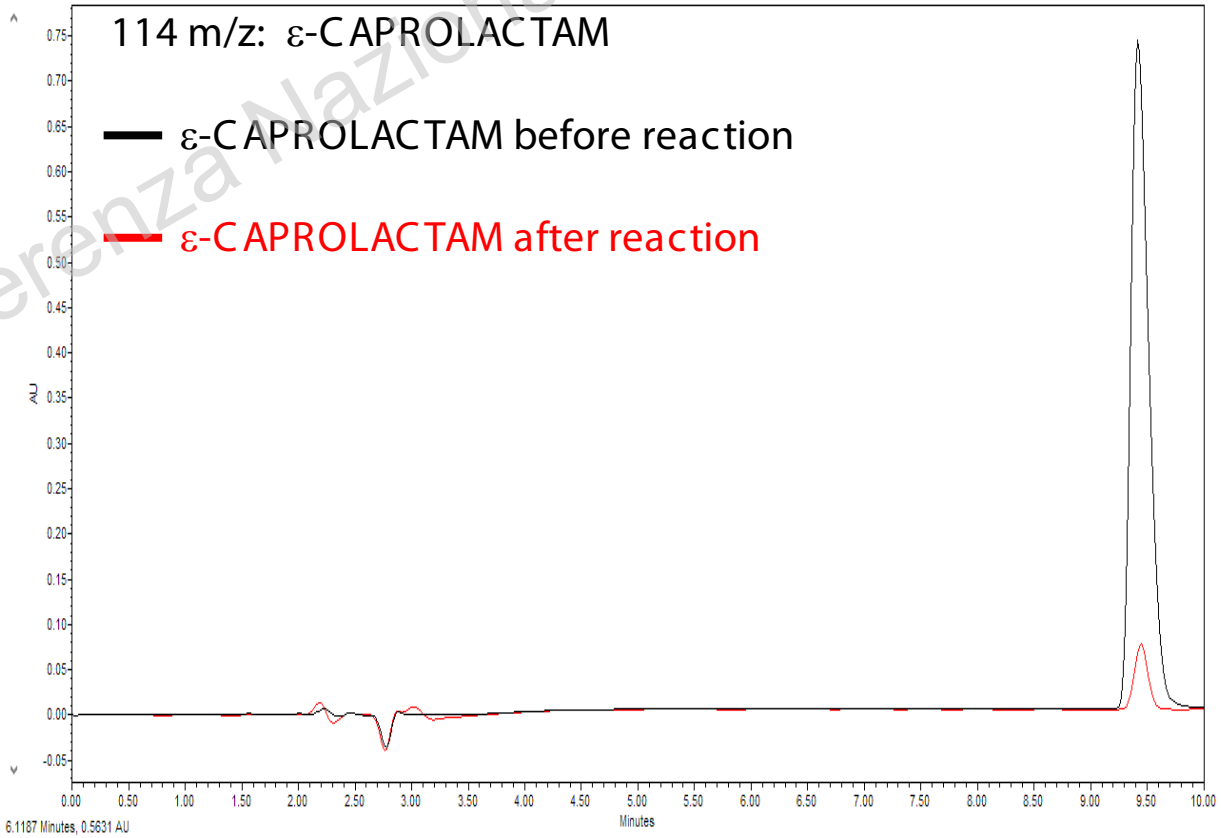


2° PHASE: ε-CAPROLACTAM REACTION

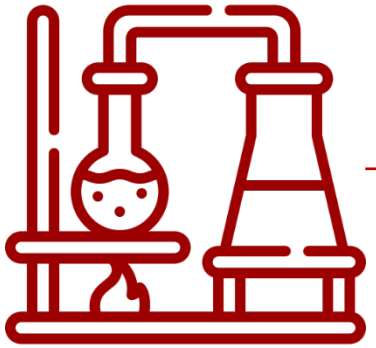
Molecular weight distribution (GPC):



Composition analysis (HPLC-MS):



Characterization of final polyols



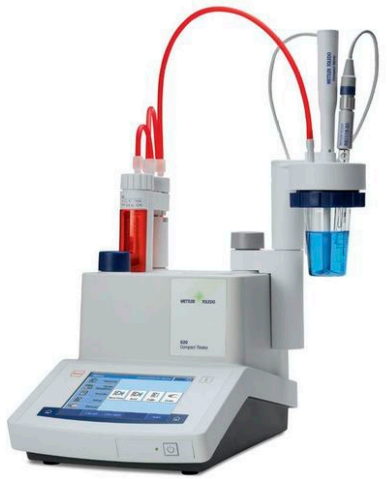
Distillation

Removal of the MEG excess to reduce HV of the obtained polyols. Subsequent evaluation of HV and %H_2O with titration.

Polyols Hydroxyl Value (HV)	Water content (%H_2O)
400-600 mgKOH/g	0,1-0,2%

→ Slight increase in products viscosity

Potentiometric titrator



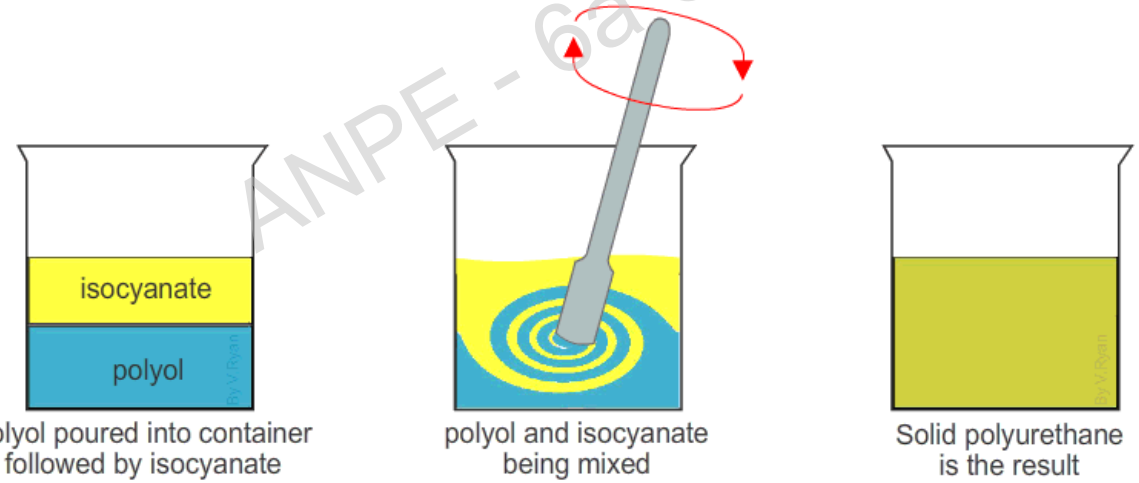
Hydroxyl value (HV)

Karl Fisher titrator

Water content

Production of new PUR foams

- New rigid foams were prepared with different recycled polyols content (25-30%) using both conventional and microwave polyols;
- Basic catalysis led to polyols that highly accelerate the reaction kinetics during foams formation;
- Only acid catalysis polyols had been used to obtain new PUR foam.



New foams characterization

COMPRESSION STRENGHT

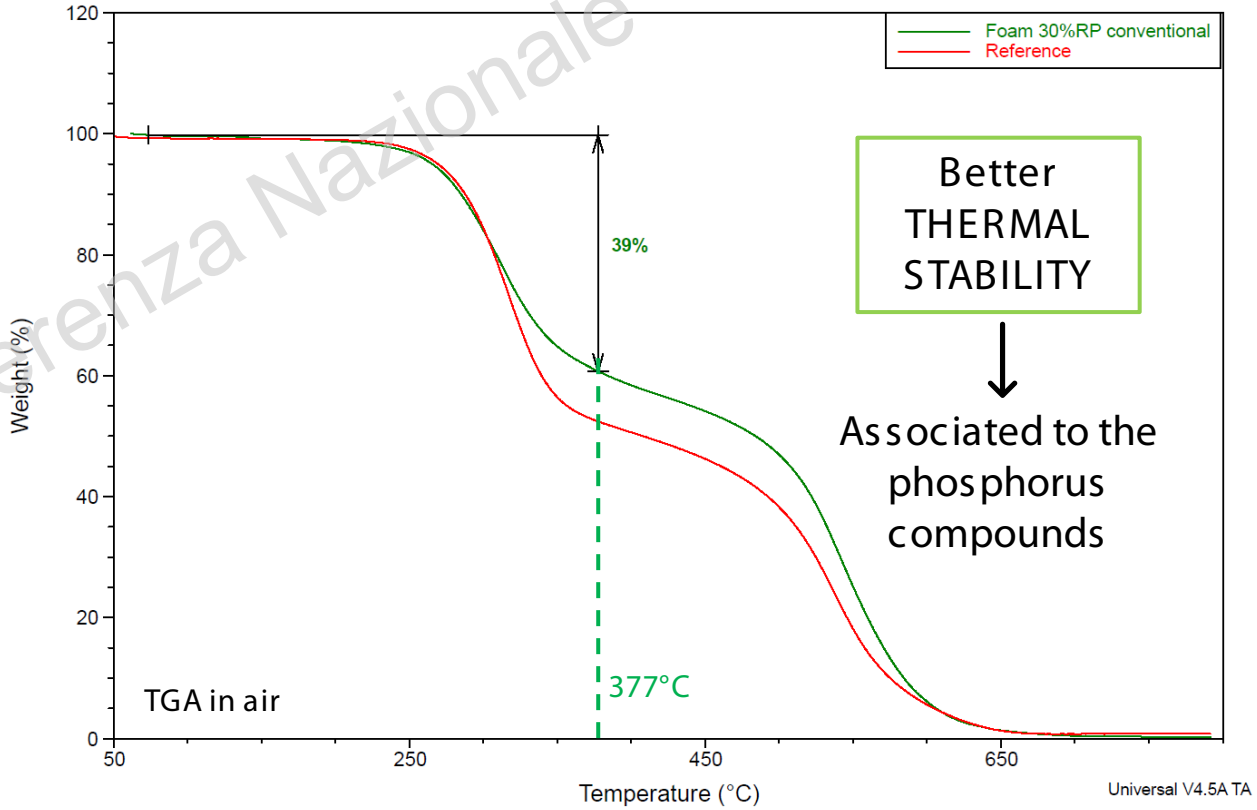
	Ref.	Conventional		Microwave	
		25RP	30RP	25RPMW	30RPMW
$\sigma_{//}$ [kPa]	358	562	463	571	495
Std Dev	20	9	20	19	21
ρ [kg/m^3]	58	66	69	65	66

Similar CONDUCTIVITY only for conventional foams

	Ref.	Conventional		Microwave	
		25RP	30RP	25RPMW	30RPMW
λ @ 10°C [mW/(m·K)]*	27,2	27,5	26,7	35,3	37,5

Max Std Dev = 0,2 mW/(m·K)
*water blown foams

PROBABLE HIGH NUMBER OF OPEN CELLS



Better THERMAL STABILITY

Associated to the phosphorus compounds

CONCLUSIONS

- Glycolysis could be a possible recycling solution for nylon 6;
- Conventional heating processes required long reaction times while the use of microwave heating reduced the reaction duration;
- For acid catalysis, the direct formation of polyester polyols terminated by phosphorus end-groups was observed;
- In basic conditions, glycolysis favored the formation of ε-caprolactam, which was then transformed into a polyol through ring opening;
- Only for conventional polyols, the recycled foams presented improved physical-mechanical properties and thermal stability compared to the virgin polyols reference foam.

Thank you for your attention

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