

Università degli Studi di Padova – Dipartimento di Ingegneria Industriale
Corso di Laurea in Ingegneria Chimica e dei Materiali

Relazione per la prova finale

**«Sviluppo di resine polisilossaniche fotocurabili
per la realizzazione di scintillatori innovativi
tramite manifattura additiva»**

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Tutor aziendale: Dott.ssa Sara M. Carturan

Coadiuvante: Dott.ssa Hanna Skliarova

Laureando: Ivan Pavone

Padova, 11/07/2023

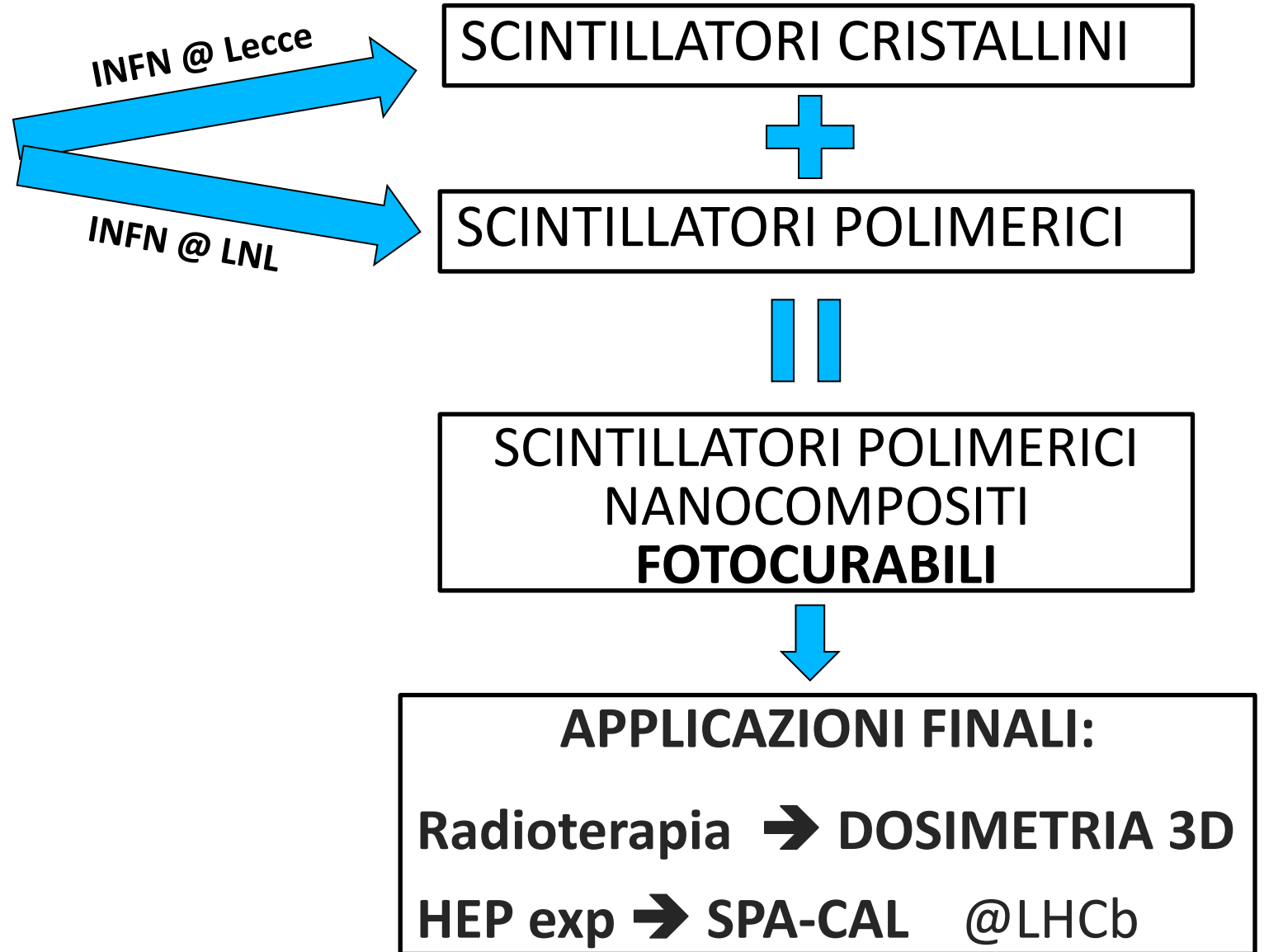
SHINE

Scintillators *Phantom*
via additive
manufacturing techniques

**RIVELATORI DI RADIAZIONI
PRODOTTI TRAMITE
MANIFATTURA ADDITIVA
FOTOINIZIATA**



Istituto Nazionale di Fisica Nucleare



SHINE

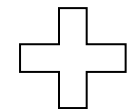
Scintillators *Phantom*
via additive
manufacturing techniques

INFN @ Lecce

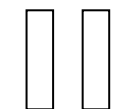
INFN @ LNL

UnIPD @ DII
Particelle α

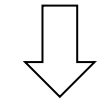
SCINTILLATORI CRISTALLINI



SCINTILLATORI POLIMERICI



SCINTILLATORI POLIMERICI
NANOCOMPOSITI
FOTOCURABILI



APPLICAZIONI FINALI:

Radioterapia → DOSIMETRIA 3D
HEP exp → SPA-CAL @LHCb

OBIETTIVI:

- PROGETTAZIONE
- SINTESI
- ANALISI
- CONFRONTO
- STAMPA



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SHINE

Scintillators *Phantom*
via additive
manufacturing techniques

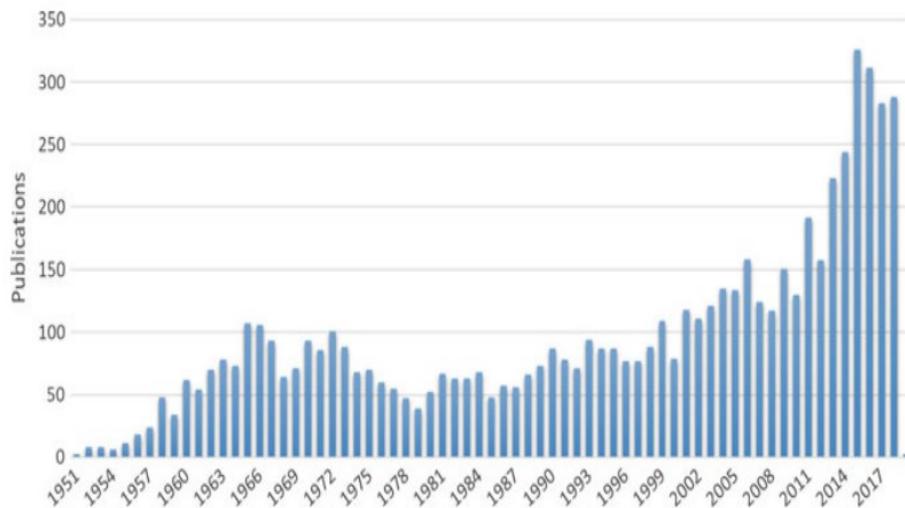
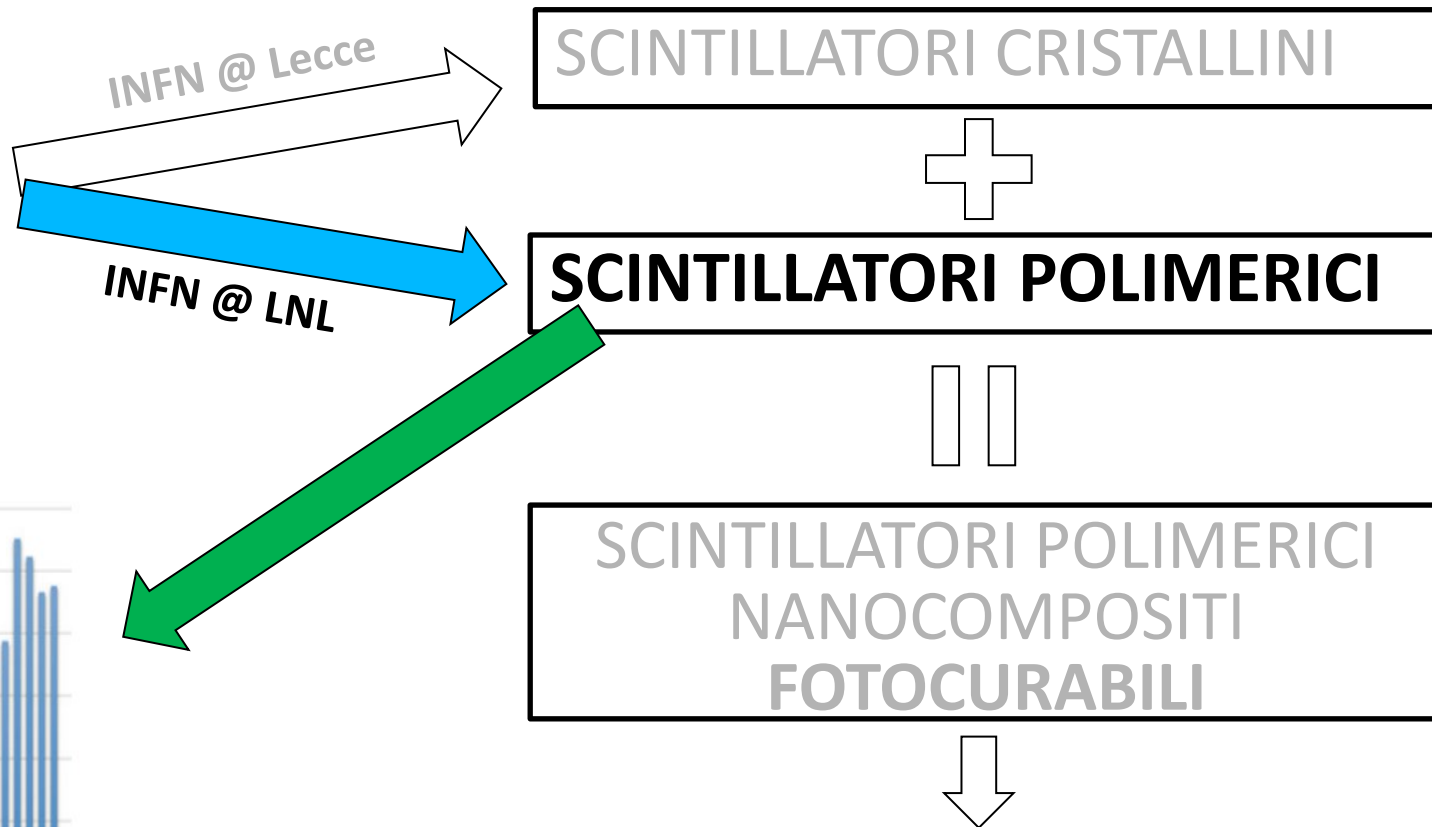


Fig. 1.2 Number of publications referring chemical modifications of plastic scintillators and sorted yearly (source SciFinder®, as of November 2019)

APPLICAZIONI FINALI:
 Radioterapia → DOSIMETRIA 3D
 HEP exp → SPA-CAL @LHCb

**SCINTILLATORI
POLIMERICI**

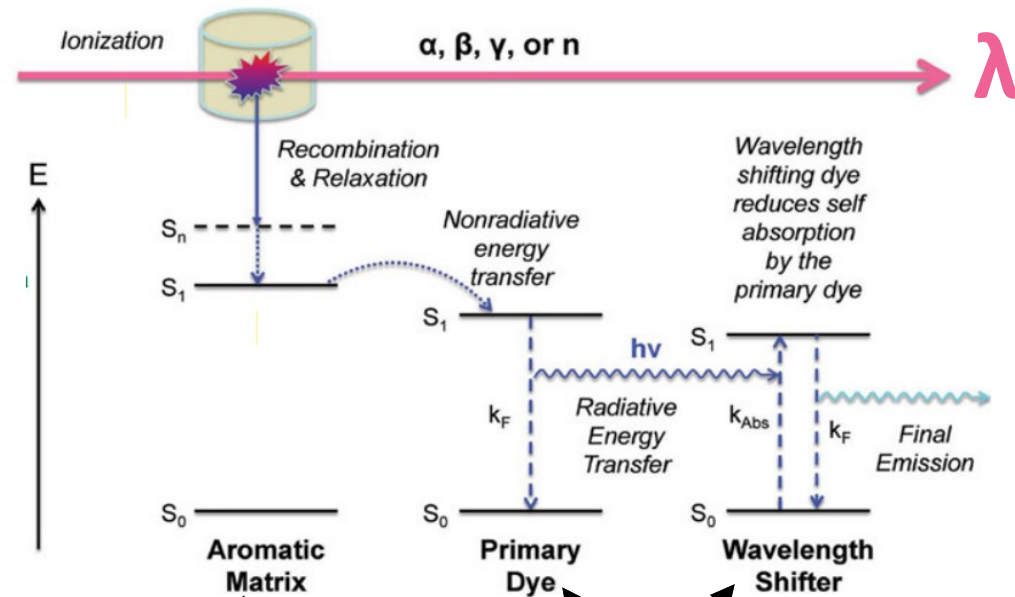


BASE POLISILOSSANO



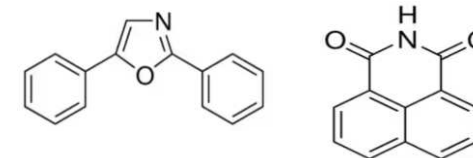
FOTOPOLIMERIZZABILI

MECCANISMO DI SCINTILLAZIONE

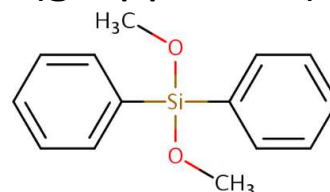


Scheme 5.1 Description of the process of light emission from a polymer-based scintillator, resulting from radiation-induced ionization

additivi fluorofori



(gruppi fenili) \uparrow \rightarrow (fluorescenza intrinseca matrice) \uparrow
 \rightarrow (solubilità additivi) \uparrow



SCINTILLATORI
POLIMERICI

→ (gruppi fenili) ↑ → (fluorescenza intrinseca matrice) ↑
→ (solubilità additivi) ↑
→ (rigidità) ↑

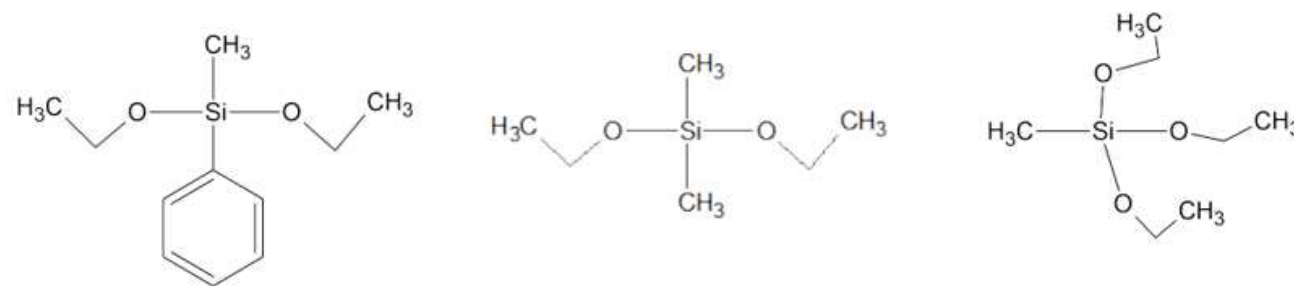


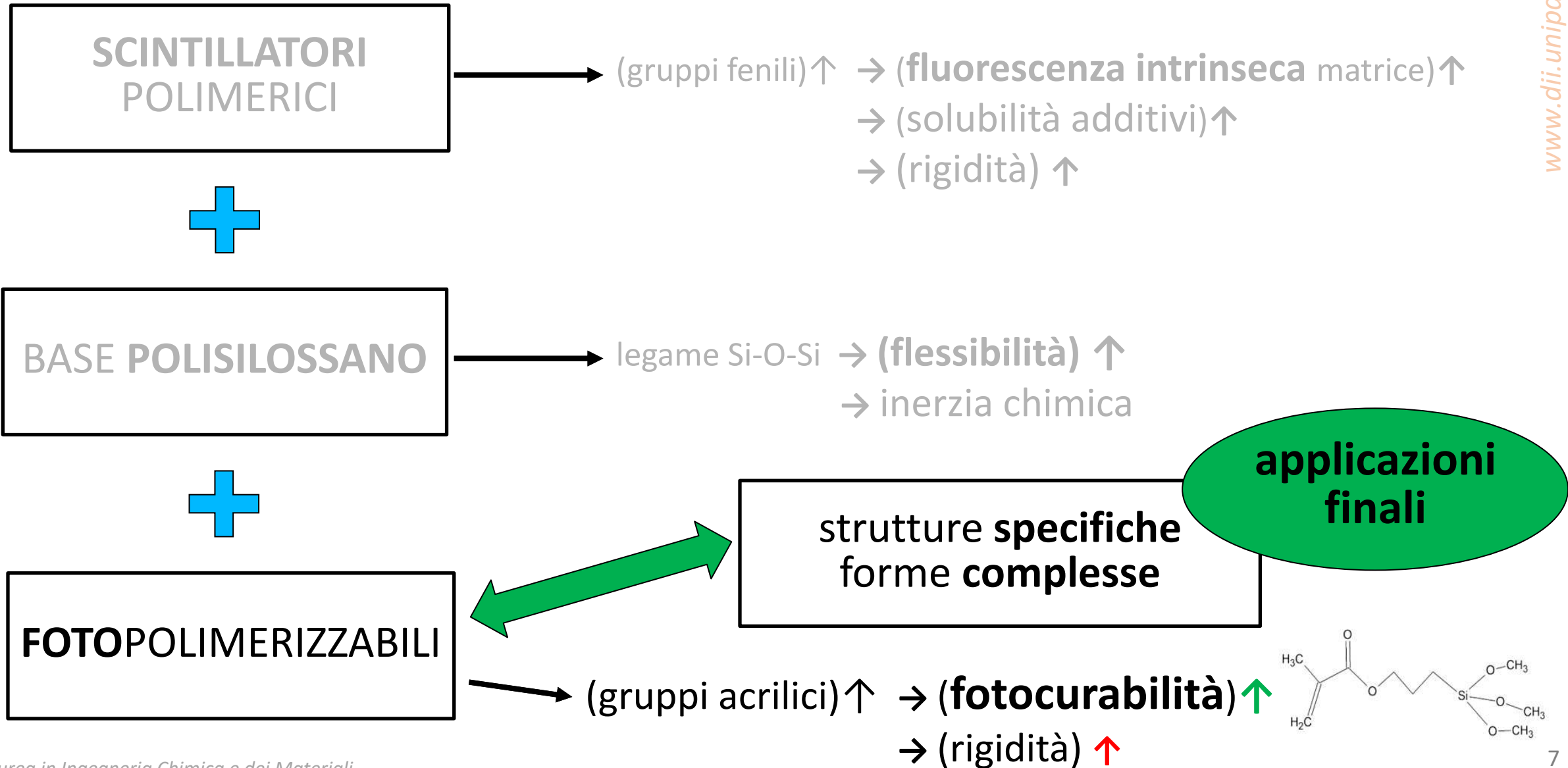
BASE POLISILOSSANO

→ legame Si-O-Si → (mobilità catena) ↑ → (flessibilità) ↑
→ inerzia chimica → protegge gli additivi dal
degrado



FOTOPOLIMERIZZABILI

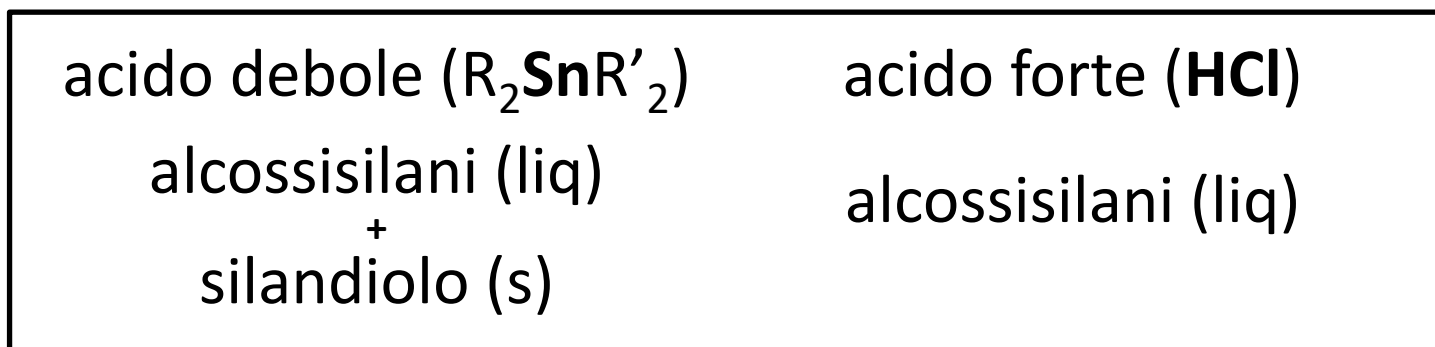




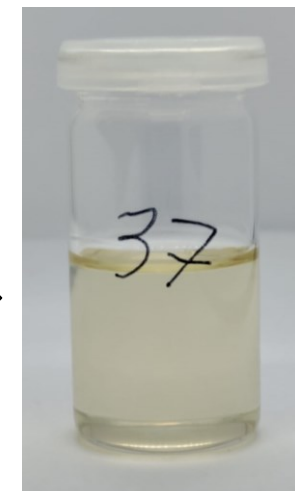
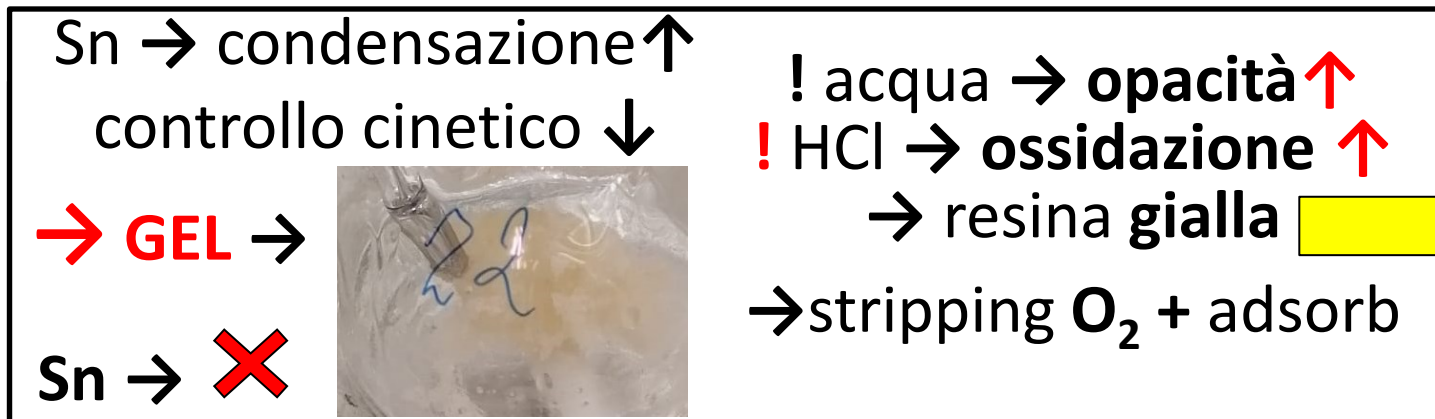
STRATEGIA



DETTAGLI



CONCLUSIONI



(i numeri
identificano
prove
progressive)

**FAMIGLIE
DI PROVE**

STRATEGIA

SOL-GEL
soluzione acquosa
(solv. 2MeTHF)
catalisi **acida**

SOL-GEL *Non Idrolitica*
soluzione anidra
(solv. 2MeTHF)
catalisi **basica**

DETTAGLI

acido debole ($R_2SnR'_2$) alcossisilani (liq) + silandiolo (s)	acido forte (HCl) alcossisilani (liq)
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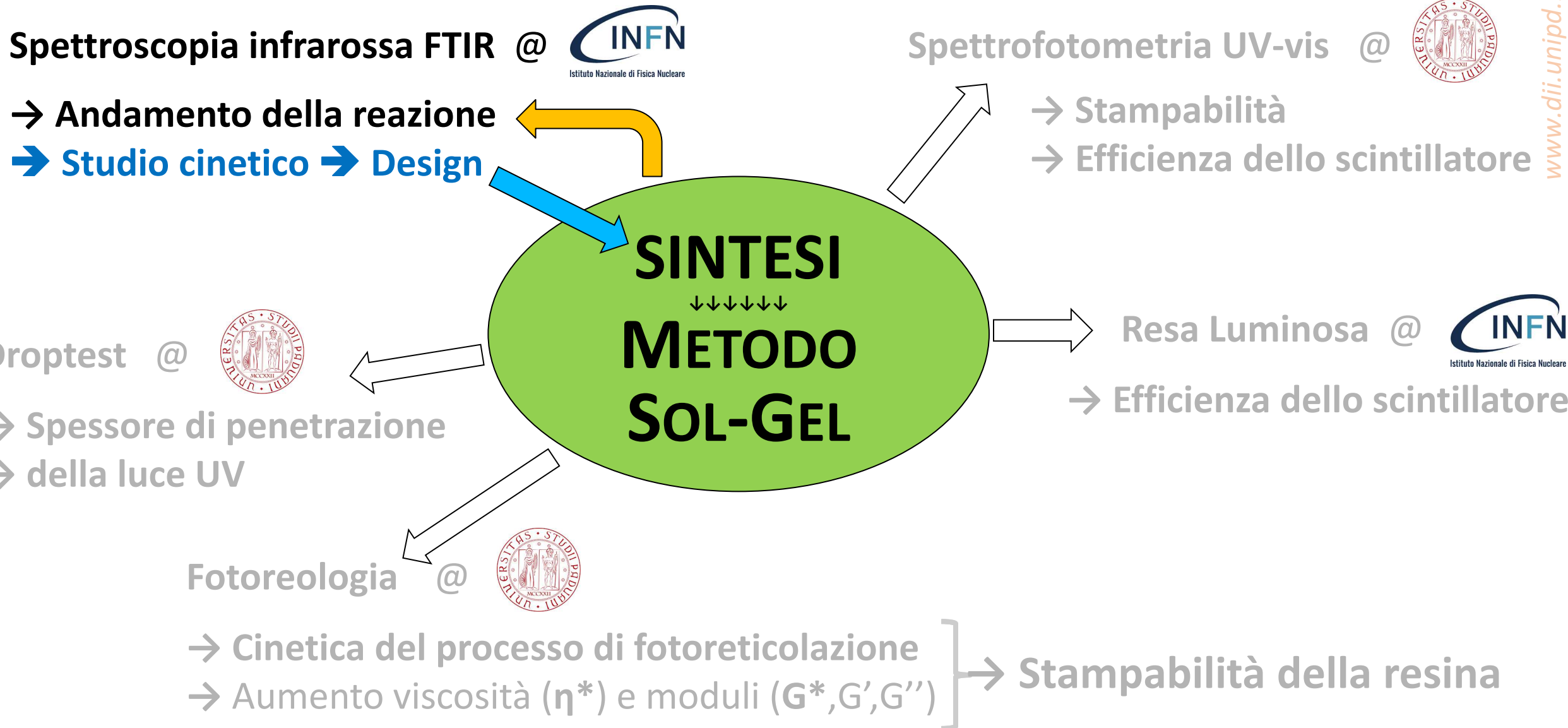
Ba(OH)₂ monoidrato
alcossisilani (liq)
+
silandiolo (s)

CONCLUSIONI

Sn → condensazione ↑ controllo cinetico ↓ prob. gelazione ↑ Sn → X	! acqua → opacità ↑ ! HCl → ossidazione ↑ → resina gialla → stripping O ₂ + adsorb
---	--

incolore →
! resina viscosa
→ distillaz. Bassa T
→ **conservare solvente**





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Spettroscopia infrarossa FTIR @



- Andamento della reazione
- Studio cinetico → Design

Spettrofotometria UV-vis @



- Stampabilità
- Efficienza dello scintillatore



Droptest @

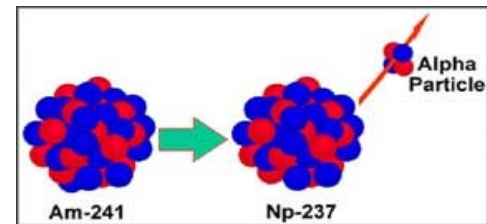


- Spessore di penetrazione
- della luce UV

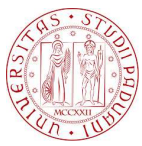
Resa Luminosa @



- Efficienza dello scintillatore

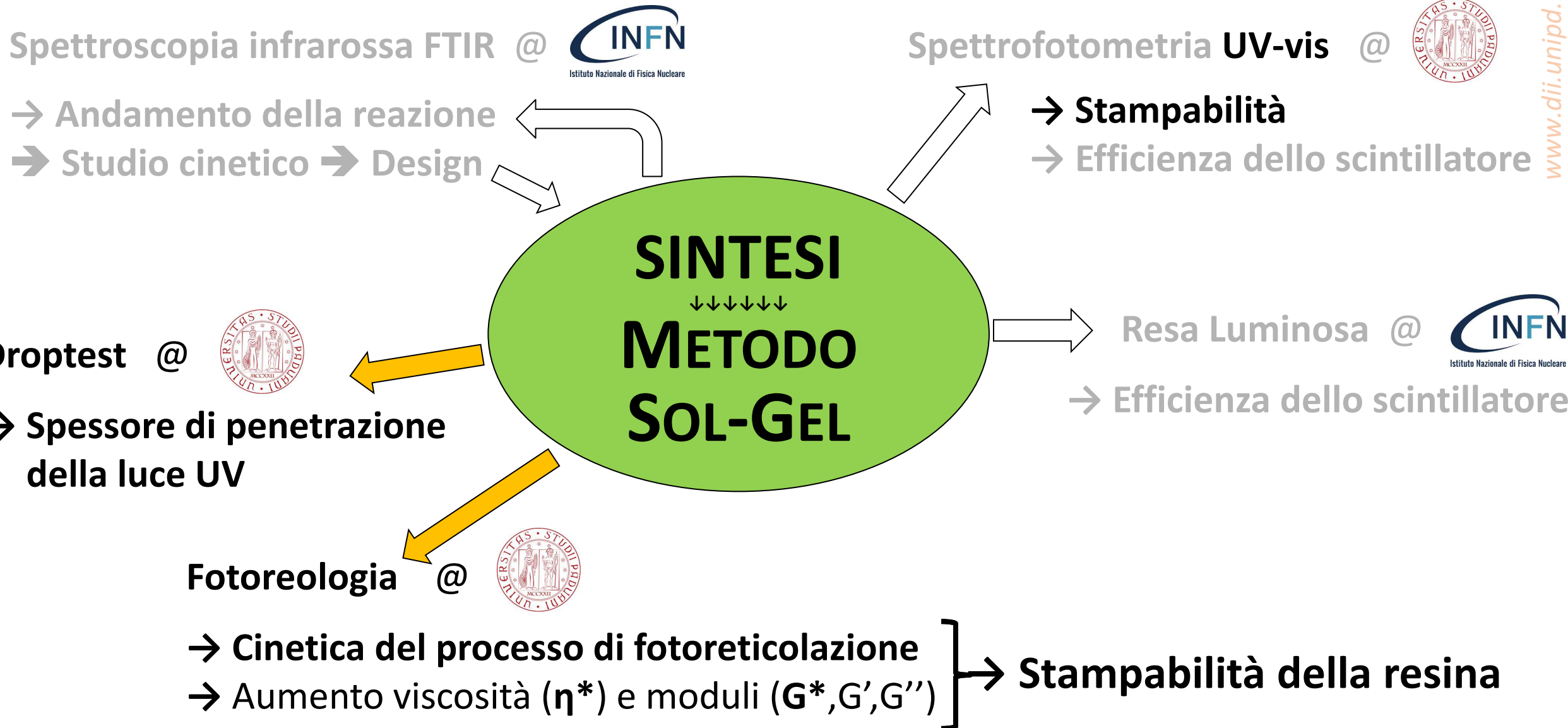


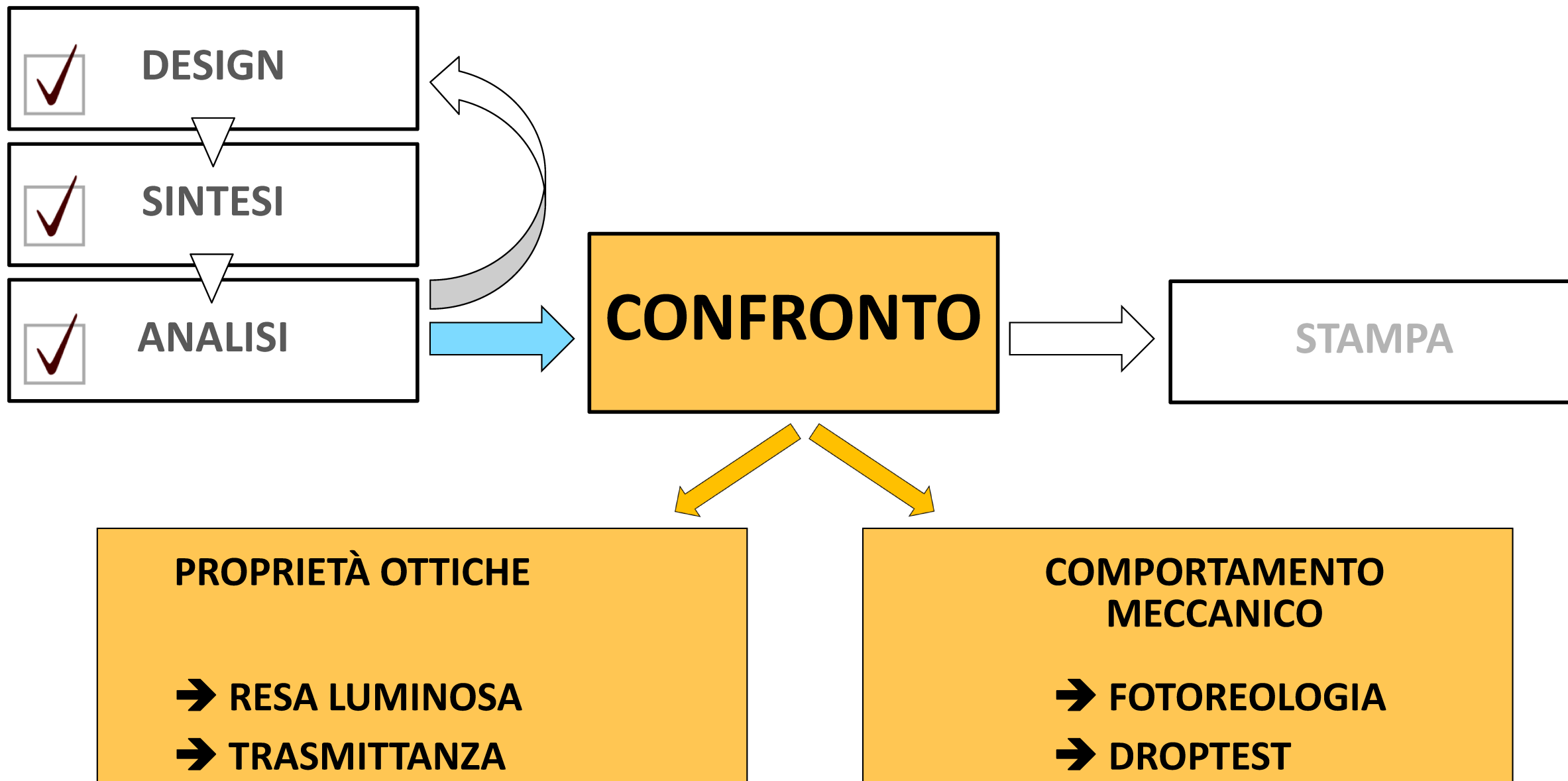
Fotoreologia @



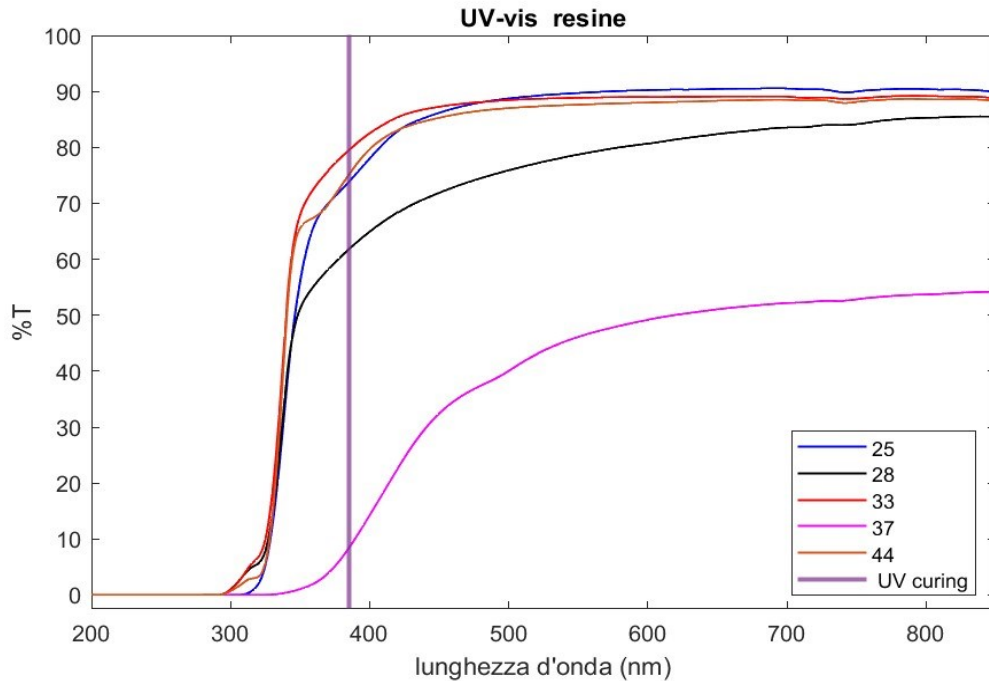
- Cinetica del processo di fotoreticolazione
- Aumento viscosità (η^*) e moduli (G^*, G', G'')

Stampabilità della resina





RESINE

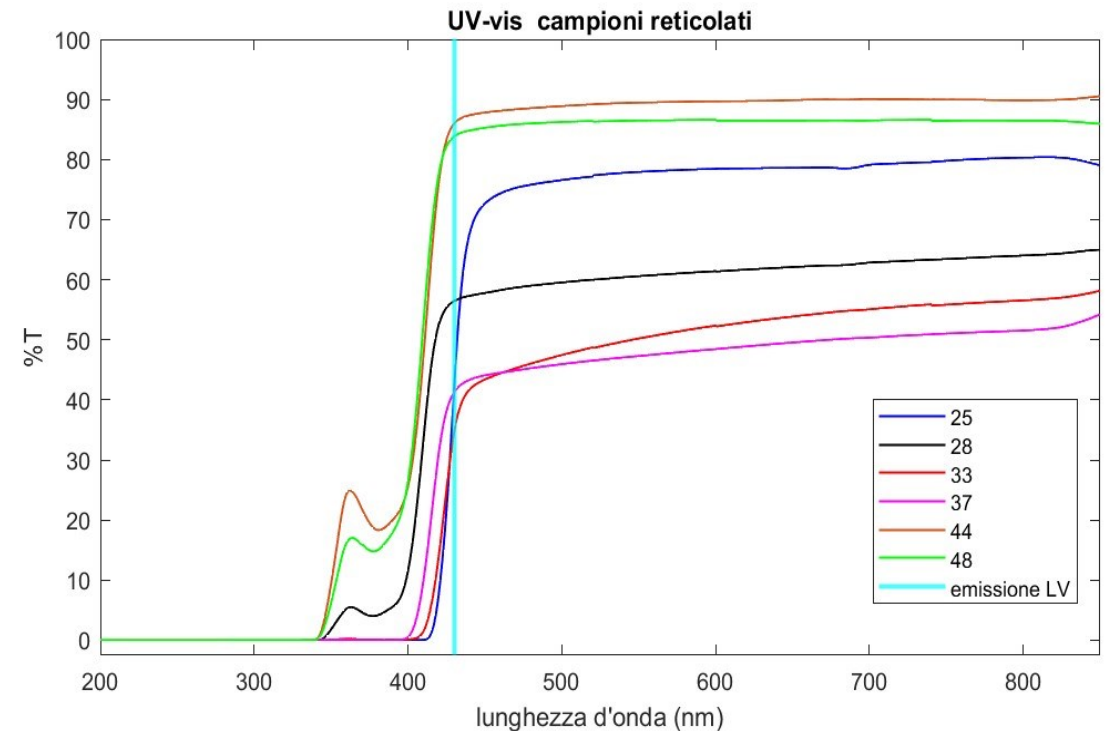


λ critica = 385 nm \Leftrightarrow λ proiettore

Resina $\%T_{(385)}$ $\uparrow \rightarrow$ (qualità di stampa) \uparrow

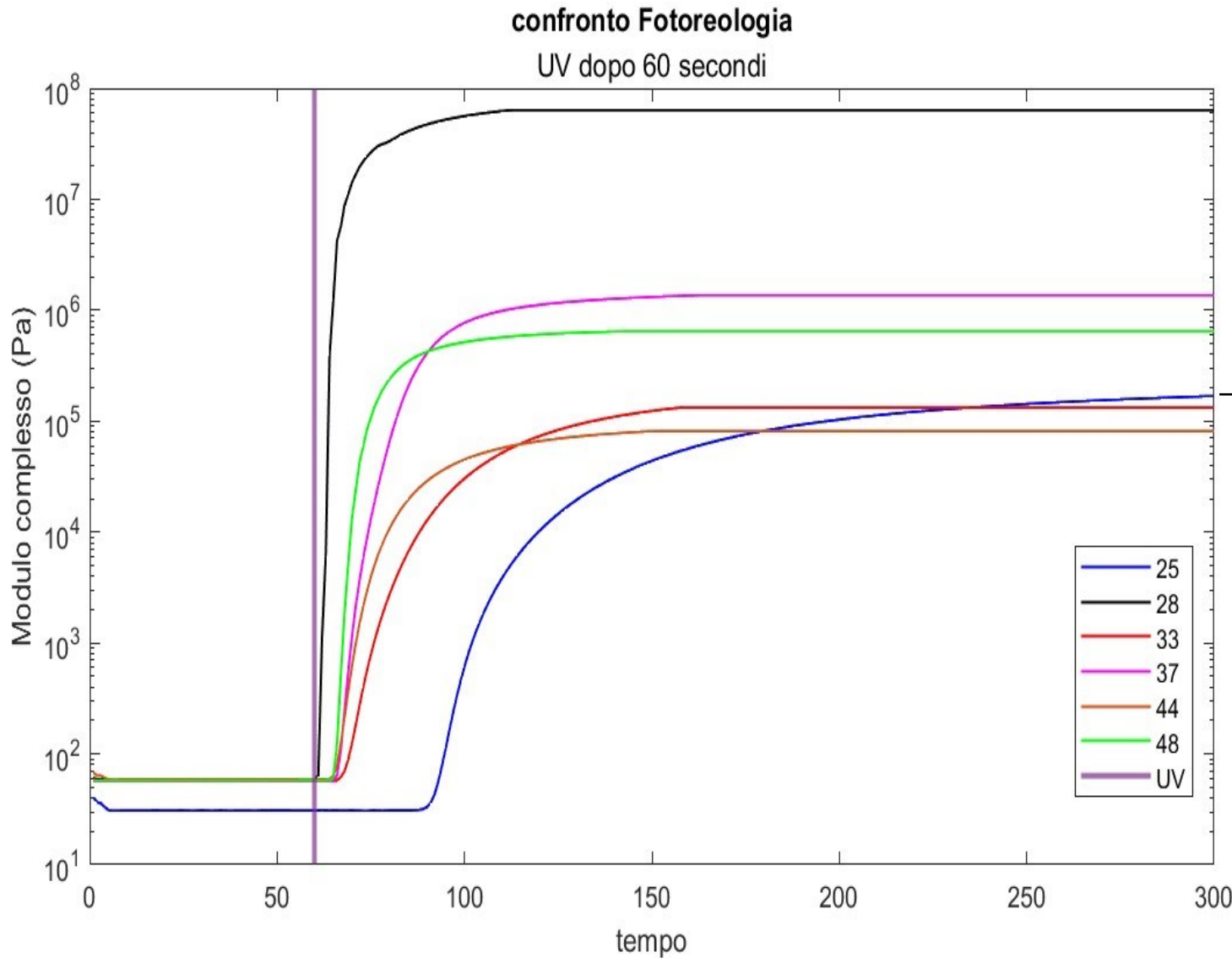
Conclusioni: resina **37** non stampabile

CAMPIONI RETICOLATI



λ critica = 430 nm \Leftrightarrow picco emissione LV

Campione $\%T_{(430)}$ $\uparrow \rightarrow$ (resa luminosa) \uparrow



DROPTTEST	volume (μL)	tempo (s)	spessore (mm)
28	50	30	1.38
33	50	30	0.6
37	50	30	0.46
44	50	30	0.49
48	50	30	0.97

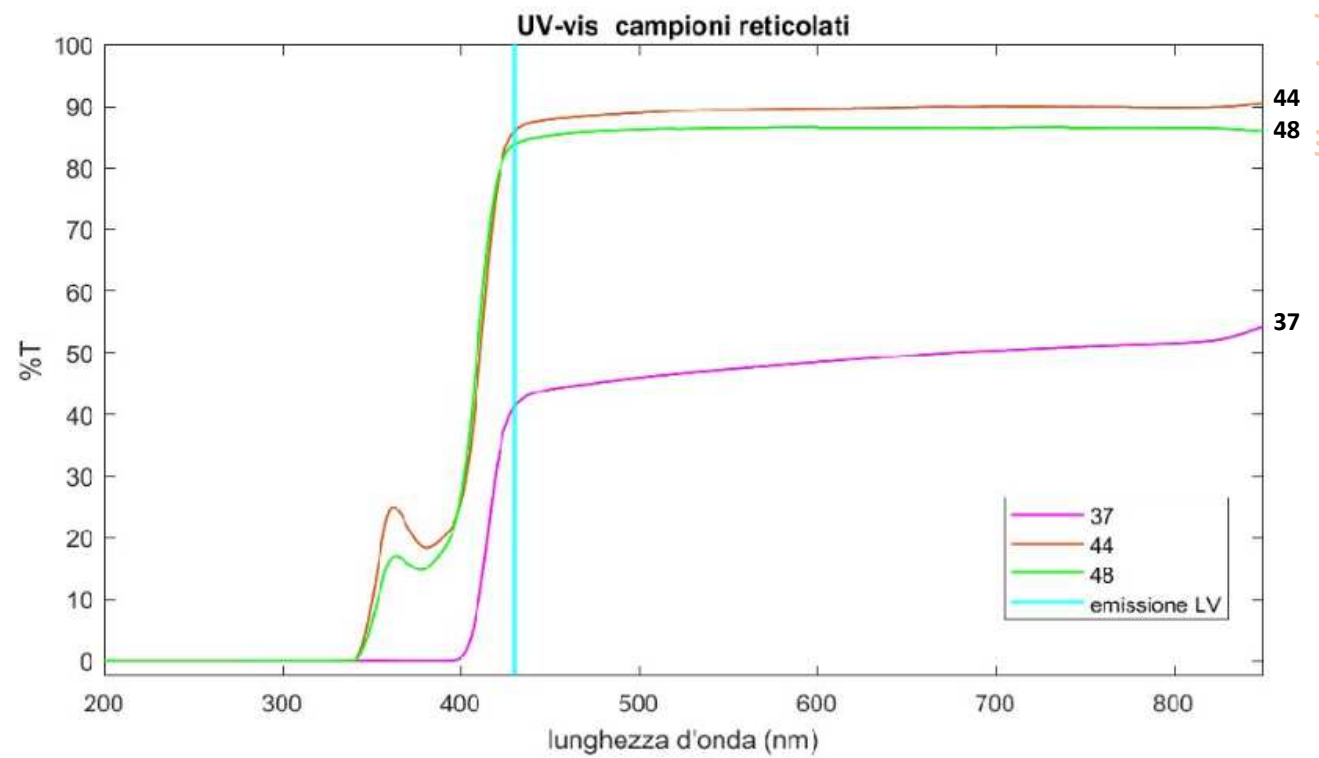
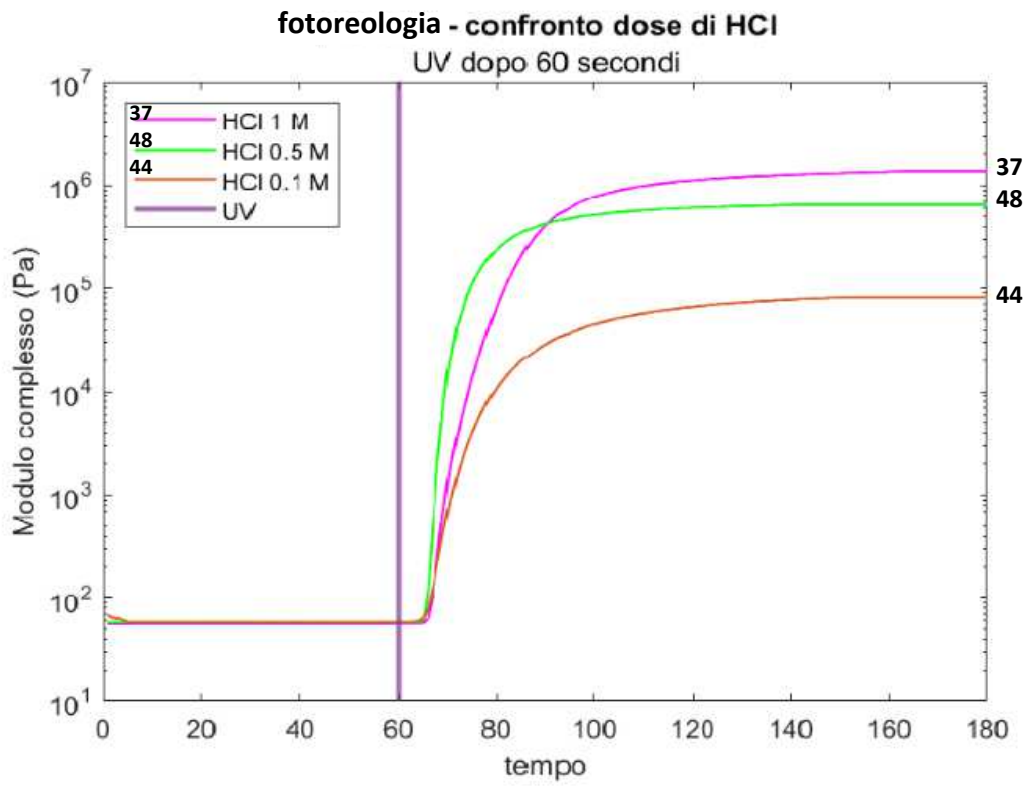
→ Resina **25**: reticolaz. inizia dopo 30 s
G* continua a salire anche dopo 240 s
e non arriva mai a plateau
(analisi ripetuta 4 volte!)

→ **Non è stampabile**

→ **RESINE SCELTE PER STAMPA:**

▪ **28** e **33** (sol-gel anidra + Ba(OH)₂)

▪ **44** e **48** (sol-gel idrolitica + ctz HCl)



(HCl)↑ → (lunghezza catena)↑ →
→ (G*)↑ ↔ (%T)↓ → (LY) ↓

metodo sol-gel	catalisi acida debole		catalisi basica anidra		catalisi acida forte		
campione n°	19	25	28	33	37	44	48
resa luce (%EJ212)	20.58	16.07	23.01	21.35	14.77	33.99	23.65
spessore (mm)	0.68	0.5	0.74	0.65	0.46	0.57	0.57
concentrazione Ctz	Sn-ctz 0.1 %VOL		Ba(OH) ₂ 0.1 %MOL		HCl 1 M	0.1 M	0.5 M

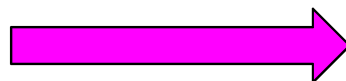
RESA LUMINOSA

STAMPA

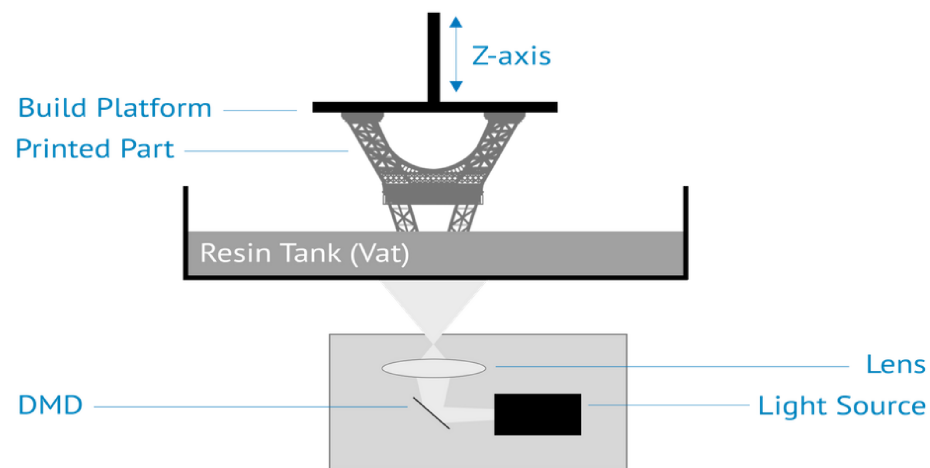
@



tecnologia **DLP**



(vat photopolymerization)



WEVOLVER

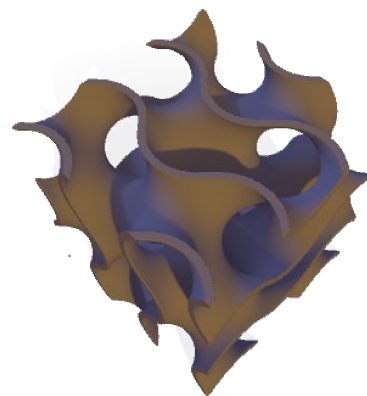
+ test SLA (res.48) *proof of concept per INFN-Lecce*

RESINE SCELTE:

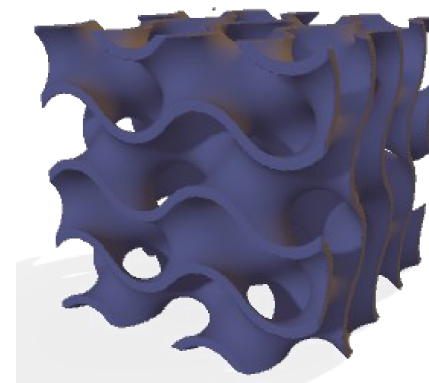
→ 28 e 33

→ 44 e 48

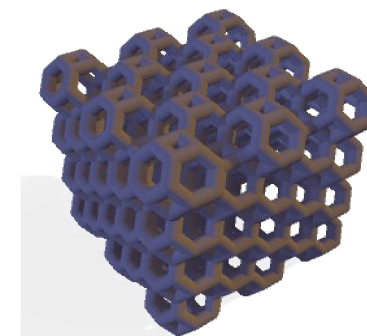
Strutture stampate:



giroide semplice



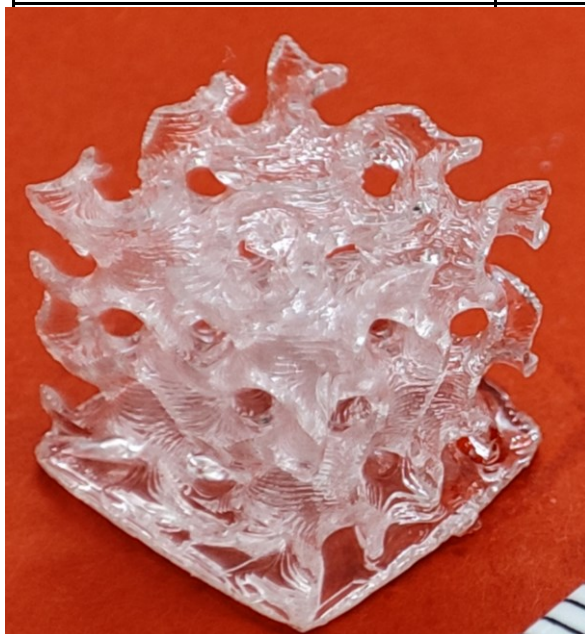
giroide complessa



cella di Kelvin

resina	28				33		
test n°	1	2	3	4	1	2	3
struttura	giroide prova	giroide semplice	giroide complessa	cella di Kelvin	giroide semplice		
spessore layer (µm)	150	150	150	150	75	50	100
tempo UV/layer (s)	4	3	3	3	10	8	10

28
T3



28
K

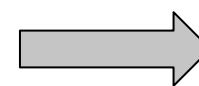


33
T3



28 stampabilità ↑
precisione ↑

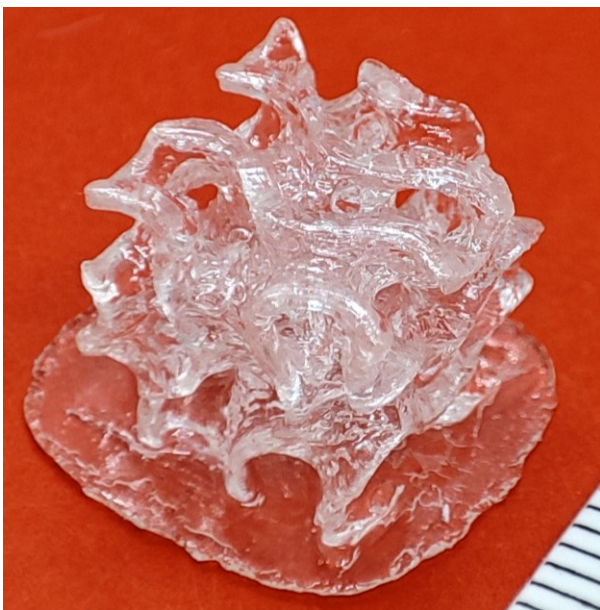
(%T) ↑ → risoluzione ↓
!! rigidità ↑



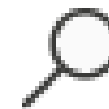
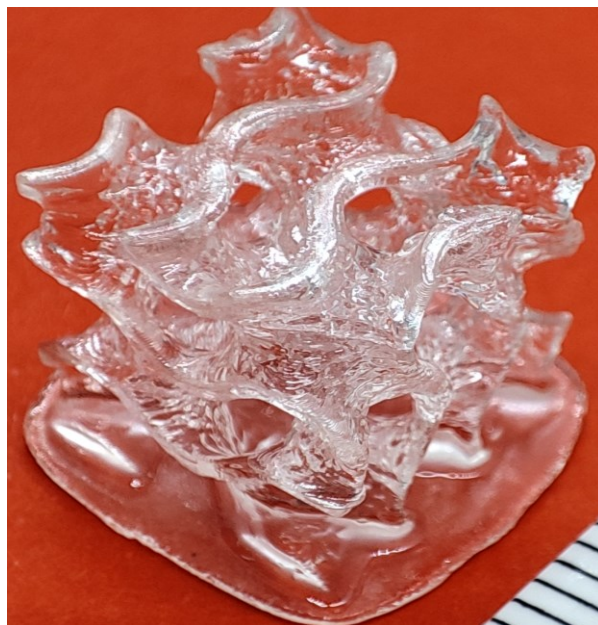
33 stampabilità ↓
flessibilità ↑

resina	44				48		
test n°	1	2	3	4	1	2	3
struttura	giroide complessa		giroide semplice		giroide semplice		
spessore layer (µm)	50	50	50	50	50	50	50
tempo UV/layer (s)	15	18	16	16	12	12	12

44
T3



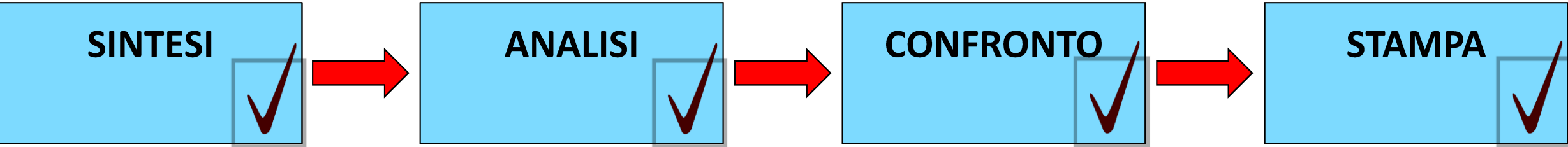
48
T2



44 Spessore layer ↓ → risoluzione ↑
!! HCl 0.1 M → fragilità ↑

→
HCl ↑

48 stampabilità ↑
flessibilità ↑



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Da qui ...

*... a
qui:*

