Materials Subproject

Towards functional polymers for nanoimprint lithography – Strategies and achievements of the NaPa Materials subproject

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Litho 2006, Marseille 26 – 30 June 2006

micro resist technology

CIDETEC

inasmet tecnalia

IPCF

IMT RAS

NaPa Emerging Nanopatterning Methods

Materials Subproject

Motivation - General tasks of the Materials subproject

- Materials are a **key factor** in the development of nanopatterning methods
  Off-the-shelf materials do not meet specific requirements of nanopatterning methods

  → Need to integrate partners into the project who develop new materials required **designed for NaPa** to exploit the potential of the techniques and to create new applications

- Focus in the **Materials subproject**
  – Nanoimprint lithography
  – Soft lithography and and self-assembly

- To **develop** materials and **provide** them to partners, close collaboration in the NIL subproject

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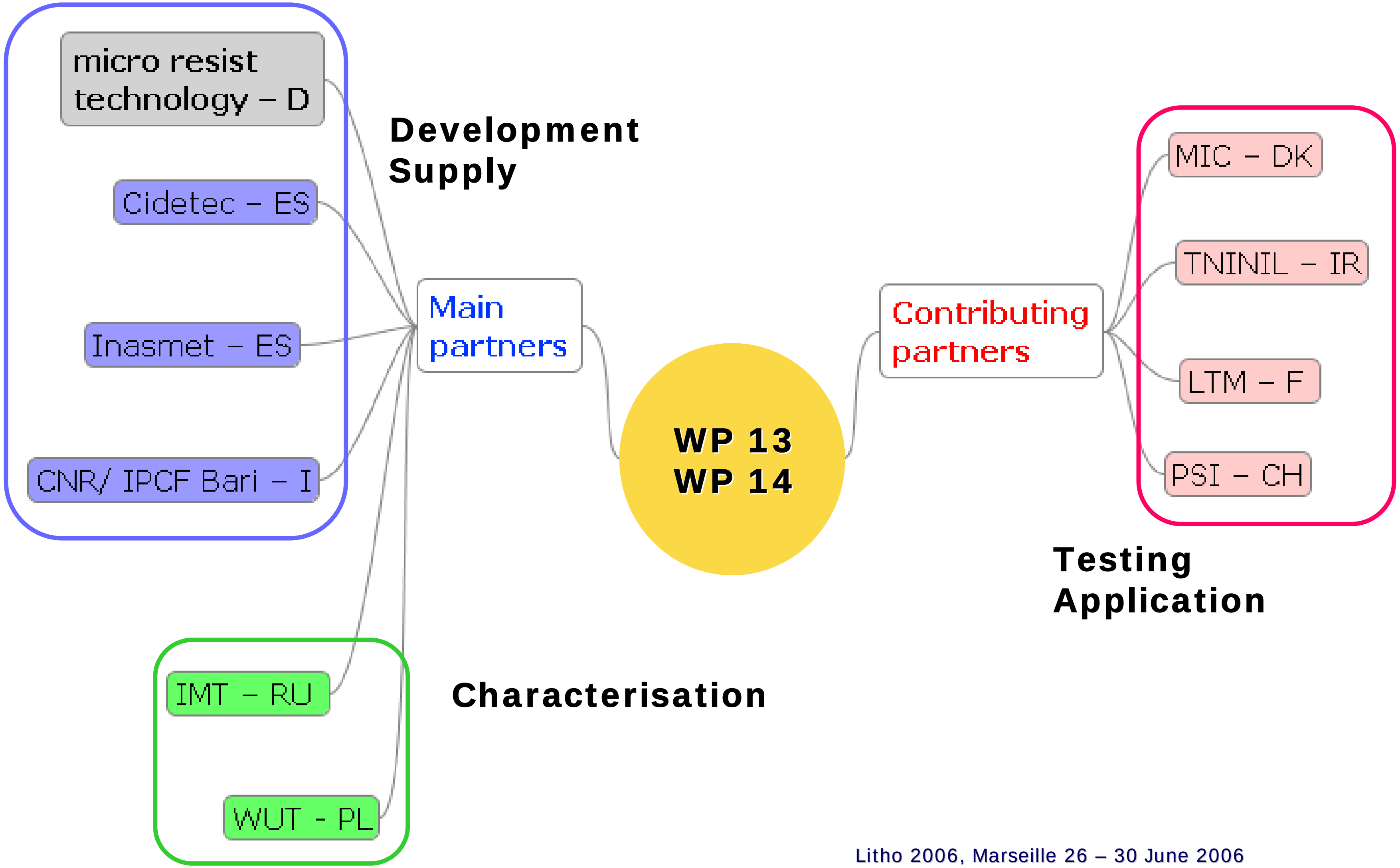
NaPa Materials subproject



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Polymer development for NIL - Strategies

Polymers for nanoimprint lithography

Thermoplastic polymers with specific/ improved imprint behaviour
→ rheological behaviour

Low imprint temperature
Low imprint time
Low imprint pressure

Curing polymers with high thermal stability

High thermal stability
→ plastic stamps

Thermoplastic polymers for specific applications
→ **functional** materials

Optical properties
Functional groups for binding biological molecules

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Outline

- **Thermoplastic polymers for NIL**
  - Mechanical behaviour
  - New developments
    Thermoplastics with improved imprint behaviour, TOPAS based polymers, polymers with narrow molecular weight distribution
- **Functionalised thermoplastics**
  - Functionalisation by synthesis - Copolymers
  - Functionalisation by surface modification of polymers
  - Functionalisation by doping of polymers with nanoparticles
- **Curing polymers**
  - Thermally curing polymers
  - Photochemically curing polymers
- **Summary**

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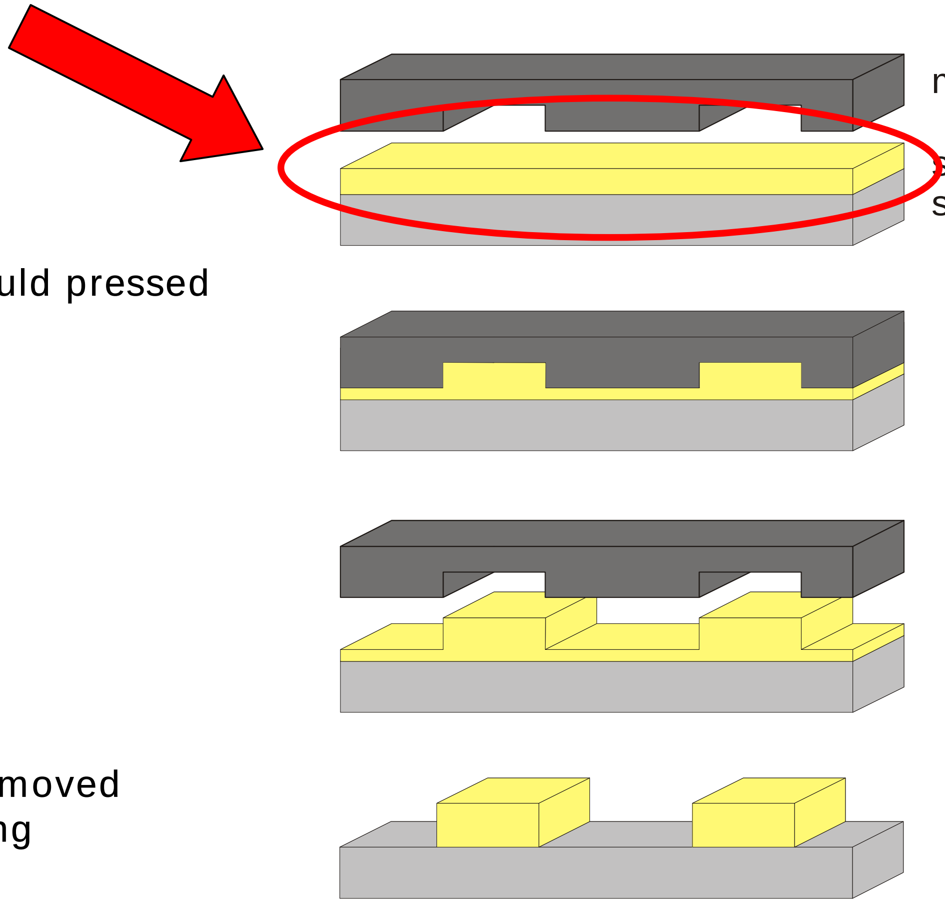
NIL process



Imprint

- Polymer solution spun on substrate

- Nano structured mould pressed into polymer @ T > T_g

- Mould removed @ T < T_g

-

Pattern transfer

- Residual polymer removed by anisotropic etching

(T_g – glass transition temperature, kind of "softening" temperature)

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Requirements for polymers for NIL

High quality amorphous films

- good adhesion to the substrate, high thickness uniformity

- Low viscosity during imprinting
- High pattern transfer fidelity, no adhesion to the mould during release
- Sufficient thermal stability in subsequent processes, e.g. RIE, lift-off
- High plasma etch resistance
  - ***allows smaller film thickness, aspect ratio and feature size***
- Soluble in non-toxic solvents, deposition by spin-coating

Thermoplastic polymers

Thermoplastic polymers specifically meeting general requirements of NIL
→ rheological behaviour

Low imprint temperature
Low imprint time
Low imprint pressure

Polymers for nanoimprint lithography

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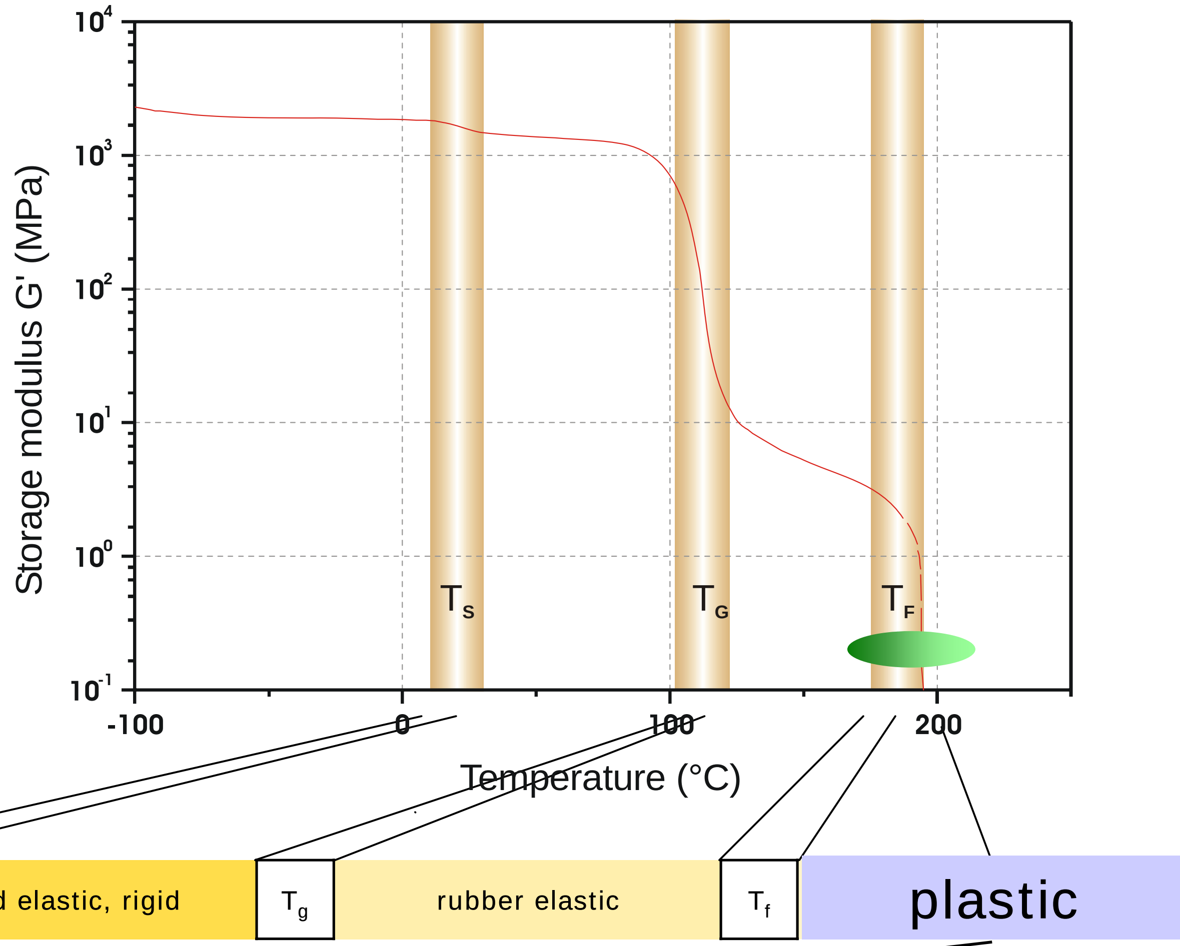
Glass transition and flow temperature of PMMA

Mechanical properties
of the polymers
- not photochemistry-
govern imprint
behaviour

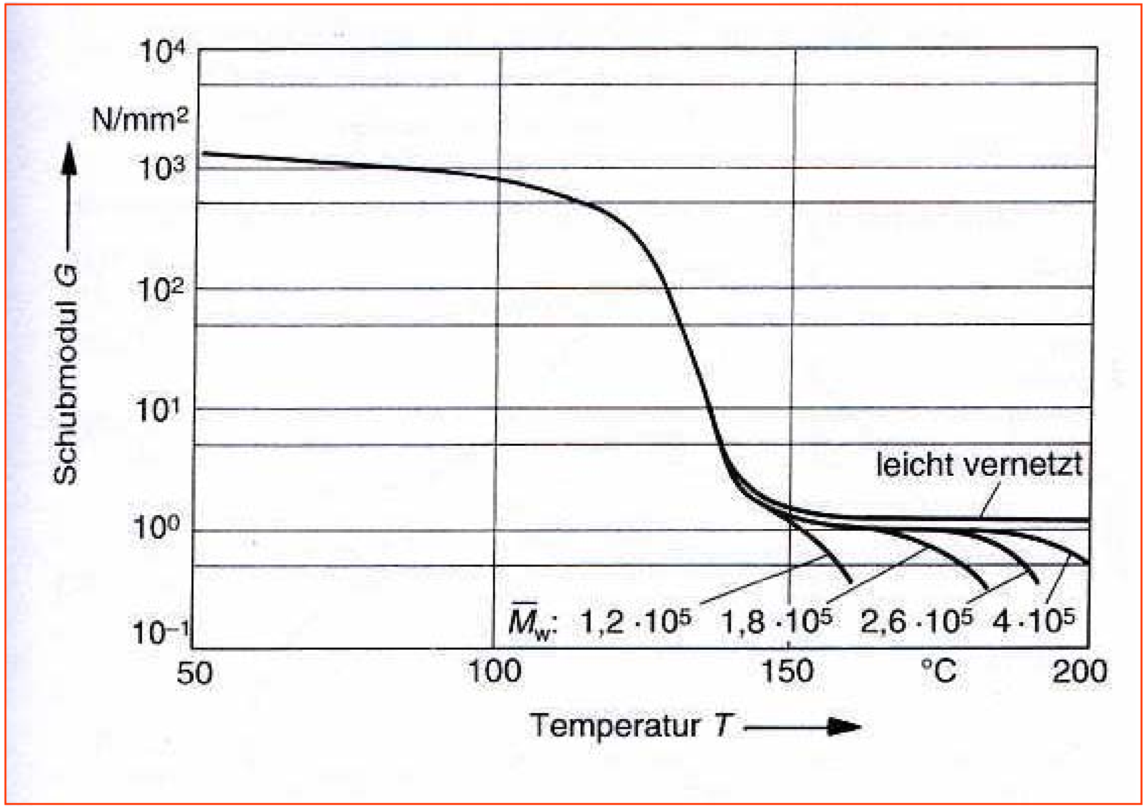
T_s	sub transition
T_g	glass transition
T_f	flow



Temperature range for NIL

Shear modulus of different molecular weight PMMAs

Flow temperature of PMMA (and other amorphous polymers) increases with increasing molecular weight.



A. Franck, Kunststoff-Kompendium,
4. Aufl., Vogel Buchverlag, Würzburg 1996, p. 255

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mr-I 7000E, mr-I 8000E - Thermoplastics with improved imprinting behaviour (1)

Thermoplastic polymers for NIL with excellent plasma etch resistance developed and provided by *micro resist technology* Berlin require **rather high imprint pressure**.

Improved imprint behaviour by redesign of the polymerisation process (mainly lower molecular weights) and the recipe of the polymer solution

mr-I 7000	60 °C
mr-I 8000	115 °C

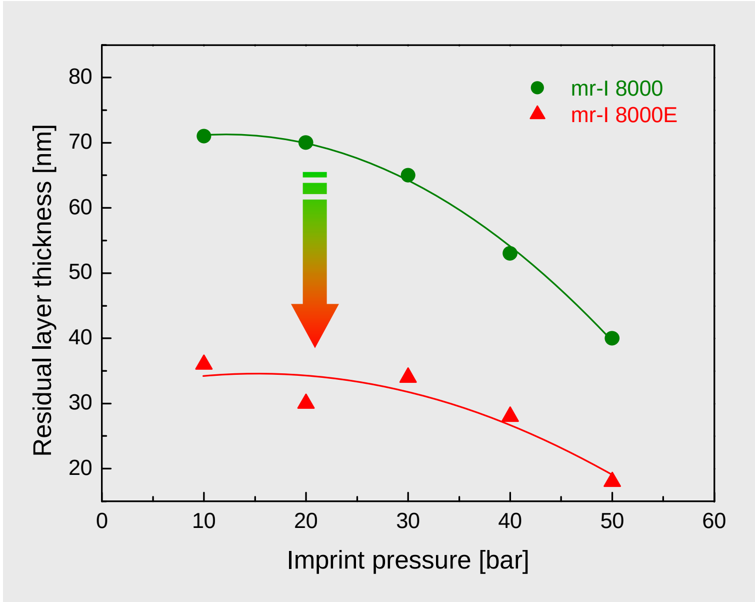
→

mr-I 7000E	60 °C
mr-I 8000E	115 °C

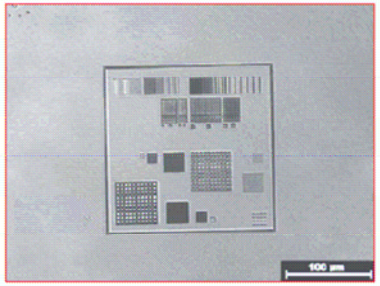
mr-I 7000E, mr-I 8000E - Thermoplastics with improved imprinting behaviour (2)

Residual layer thickness as a function of imprint pressure
Film thickness: 200 nm
Imprint: 10 s @ 160 °C, incomplete filling of stamp cavities

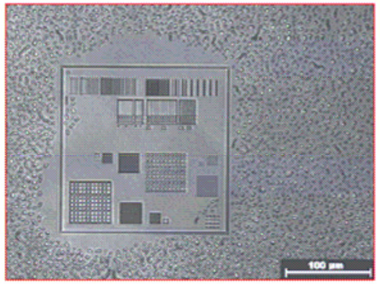
- Lower imprint pressure
- Lower residual layer thickness
- Shorter cycle times due to faster imprint



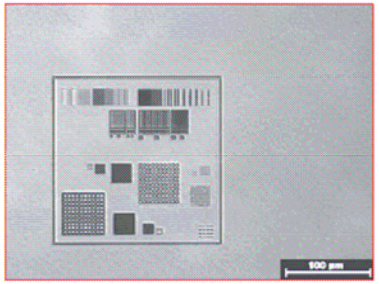
Defect-free imprints at lower pressure



mr-I 7000
130 °C, 3 min,
50 bar
no defects



mr-I 7000
130 °C, 3 min,
20 bar
insufficient polymer flow



mr-I 7000E
130 °C, 3 min,
20 bar
no defects

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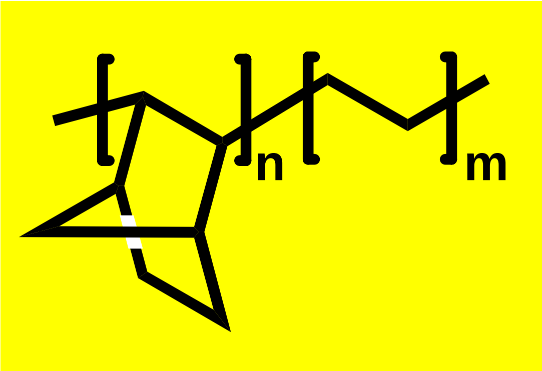
TOPAS polymers for NIL

- COC: cyclic olefinic copolymer (norbornene and ethylene)
- Attractive properties:
  - **very unpolar**
  - very low water absorption
  - high optical transparency (> 300 nm)
  - high chemical resistance
  - low surface energy
  - high plasma etch resistance

Finding solvent system giving homogeneous and stable solutions - Challenging task



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Cyclic Olefin Copolymer TOPAS for nanoimprint lithography for bio-applications

Homogeneous spin-coating of Topas

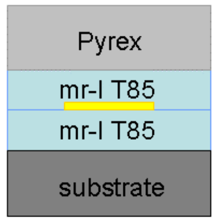
Control of Topas surface on wafer substrates

Commercialisation of Topas solutions:

- **mr-I T85** with Topas grade 8007
- **mr-I T65** with Topas grade 9506

***Applications**:*

- *Lab-on-a-chip microfluidic system for absorption measurements*
- *Plasmon polariton wave guide components*
- *Pattern transfer for photonic crystal devices*



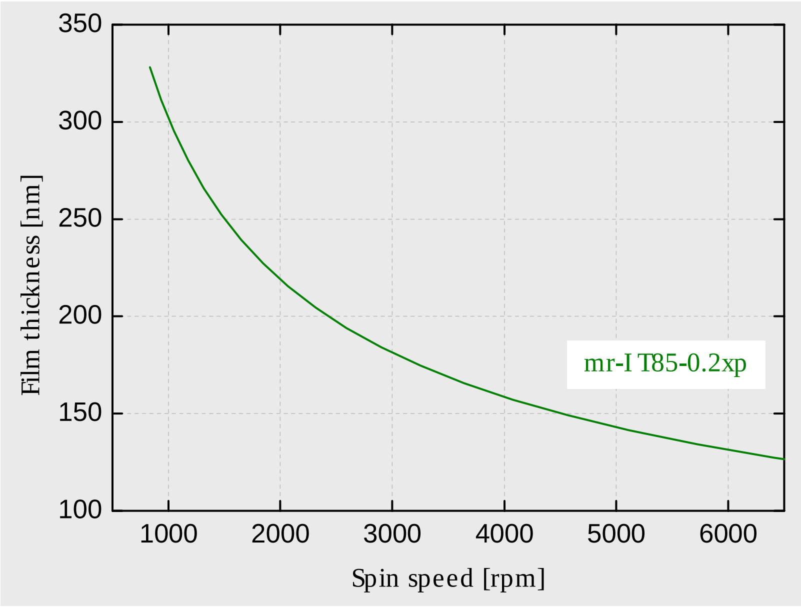
(*in Collaboration with MIC*)

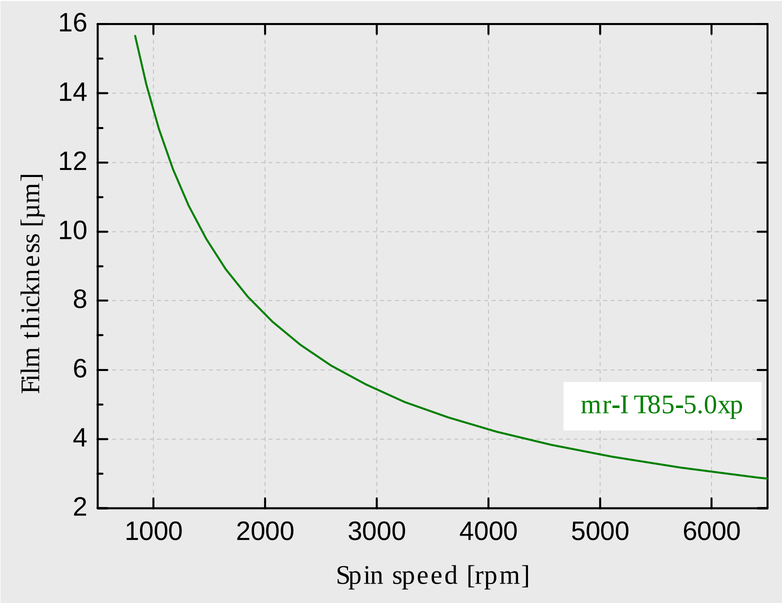
TOPAS film thicknesses

Commercialisation of Topas solutions:

- **mr-I T85** with Topas grade 8007
- **mr-I T65** with Topas grade 9506

Spin curves: mr-I T85 in solvent system 1





Well defined thermoplastic polymers by ATRP

ATRP - **Atom transfer radical polymerization**

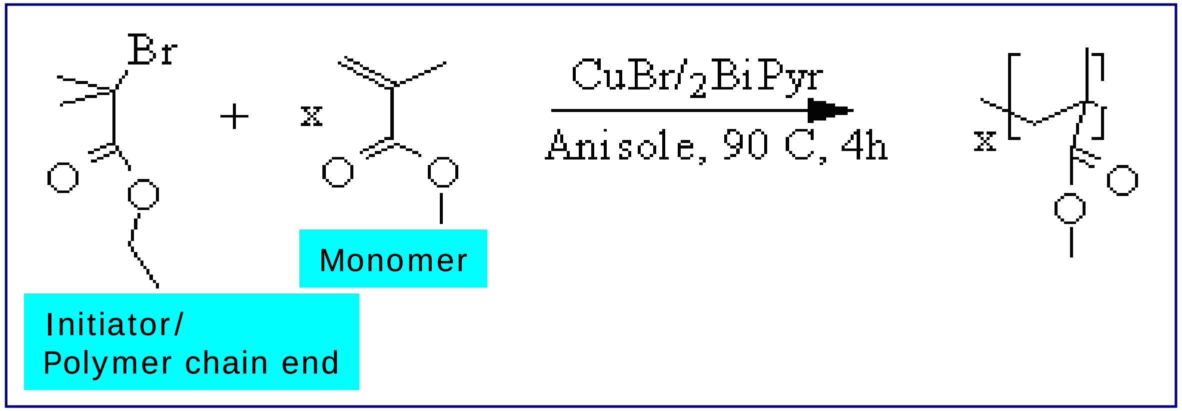
Variant of living polymerization

- Versatility
- Many possibilities to create various polymer architectures
  - block polymers
  - graft polymers
  - dendritic polymers
- Control of the molecular weight
- Low polydispersity
- A lot more possibilities for tailoring polymer properties, when using different monomers (copolymerisation)

→ **powerful method for tailoring polymer properties**

Synthesis of low polydispersity homo-polymethacrylates

ATRP conditions:



Polymer	Molecular weight g/mol	Polydispersity
Poly(methyl methacrylate)	15,000	1.15
Poly(methyl methacrylate)	24,000	1.15
Poly(methyl methacrylate)	50,000	1.2
Poly(aromatic methacrylate)	13000	1.10
Poly(aromatic methacrylate)	16500	1.4
Poly(aromatic methacrylate)	33000	1.2
Poly(aromatic methacrylate)	89000	1.2

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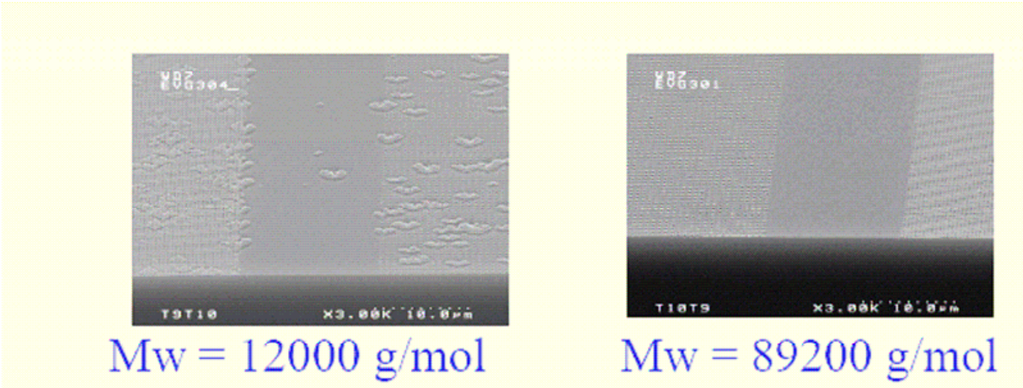
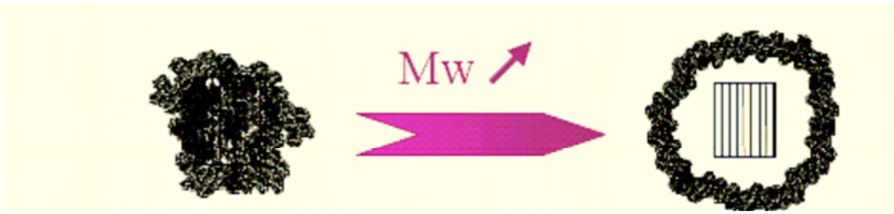
Influence of molecular weight on imprinting

Imprinting temperature : T_g+20 K





When imprinted at low temperature, then less defects induced by capillary effects with increasing molecular weight

(*N. Chaix, C. Gourgon, S. Landis, C. Perret (LTM), NNT 2004*)

Functionalised polymers

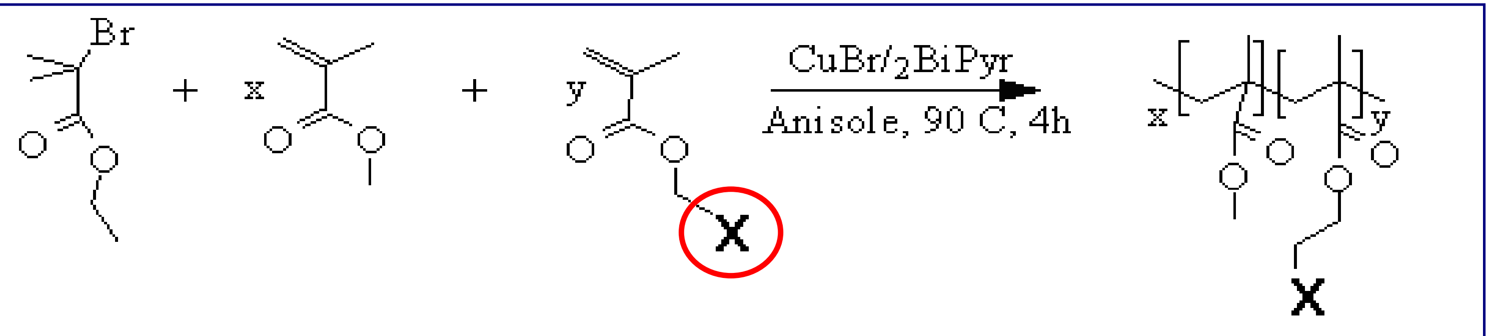
Polymers
for
nanoimprint lithography

Polymers for specific applications
→ **functional** materials

Optical properties
Functional groups for binding biological molecules

Materials Subproject

Functionalised random copolymers



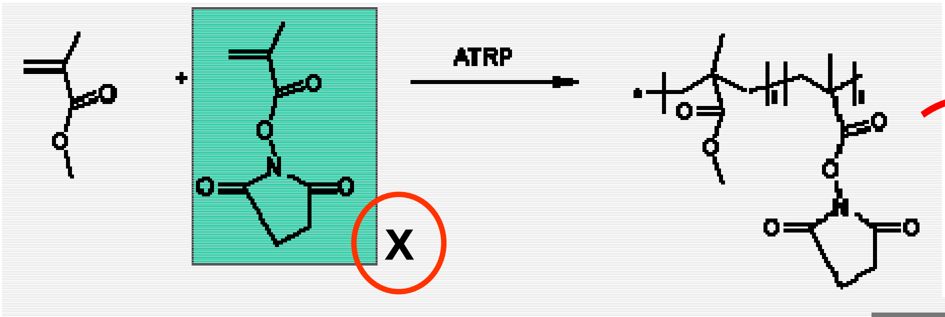
Polymer	Molecular weight g/mol	Polydispersity
Poly(methyl methacrylate-co-methacrylic acid)	15,000	1.2
Poly(methyl methacrylate-co-dimethyl aminoethyl methacrylate)	18,000	1.2
Poly(methyl methacrylate-co-perfluorinated methacrylate)	15,000	1.2
Poly(methyl methacrylate-co-glycidyl methacrylate)	20,000	1.2

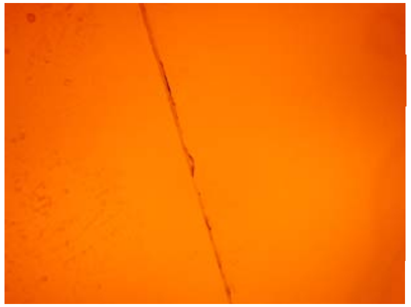
X:

- carboxylic acid
- tertiary amine
- perfluorinated alkyl
- glycidyl
- hydroxy groups
- …

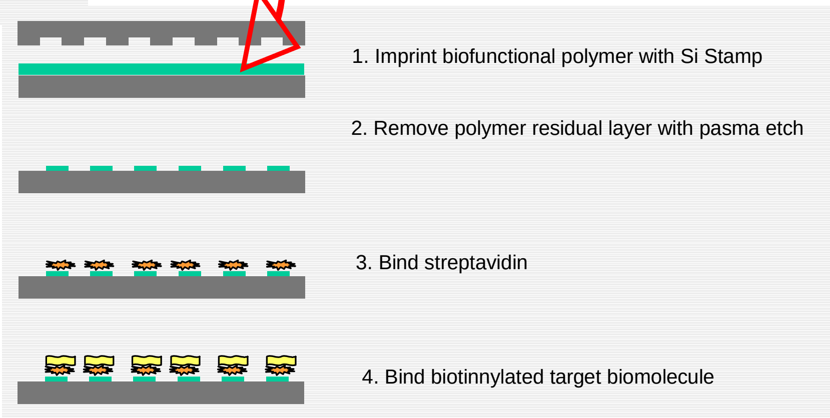
Functional random copolymers
Example: Poly(MMA-succinimidyl methacrylate)

Polymers for biological applications by introduction of functional groups





Fluorescence Microscopy of polymer with bound streptavidin



Envisaged 4 step-nanolithography method using functionalised polymer

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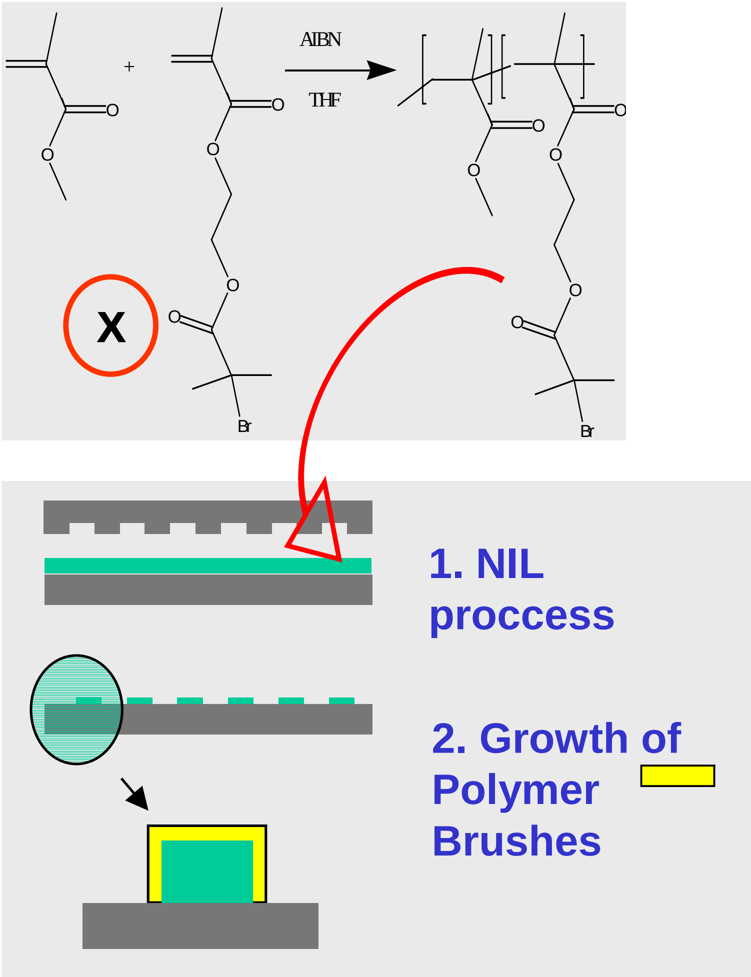
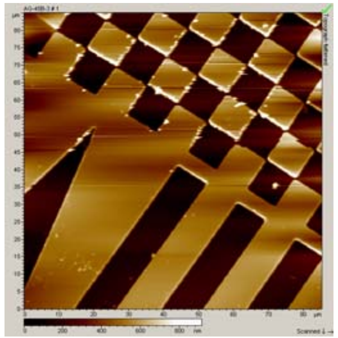
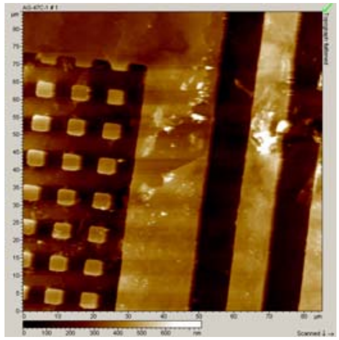
Nanoimprinted surface modification by polymer brushes



(in collaboration with TNINIL)

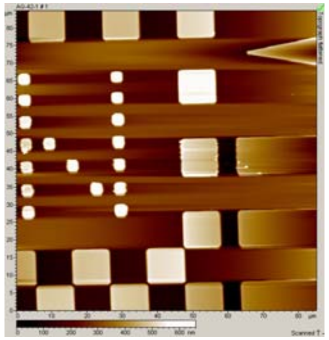


Water contact angle of imprinted PMMA copolymer: 88º



Surface modification of nanoimprinted polymer by growing hydrophilic polymer brushes: Based on Sulfopropyl methacrylate

Water contact angle: 34.4º



Surface modification of nanoimprinted polymer by growing hydrophobic polymer brushes:Zonyl fluoromonomer

Water contact angle: 115º

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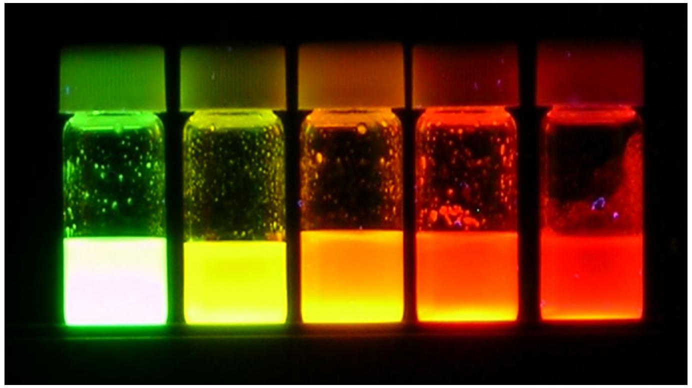
New nanocrystal/polymer based materials for NIL

Why synthesis and functionalisation of colloidal nanoparticles for incorporation in thermoplastic and curing polymers?

Tuning of functional properties

- Optical absorption and emission
- Mechanical Stability
- Conductivity
- Processability
- ...



Size dependent luminescent CdSe NCs

→ Potential for new permanent applications

Materials Subproject

What kind of Nanoparticles?

Luminescent NCs: •CdS NCs;

•CdSeNCs;

•CdSe@ZnS NCs

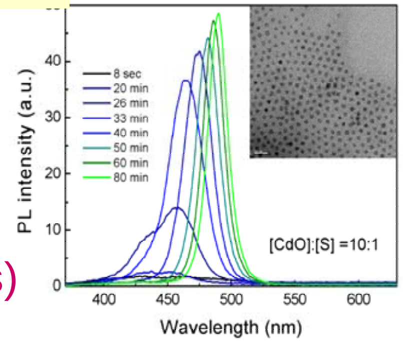
Oxide NCs: •TiO_2 NCs (dots and rods)

Metal NPs: •Au nanodots and nanorods

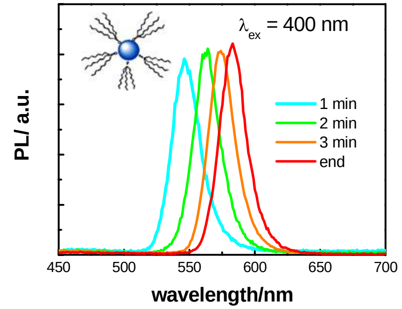
Metal oxide composites: •TiO_2/Au

•TiO_2/Ag

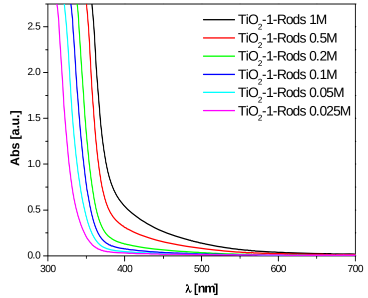
CdS NCs



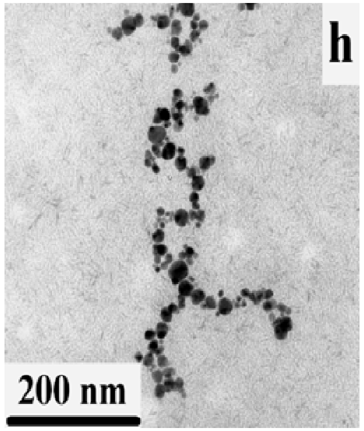
CdSe@ZnS NCs



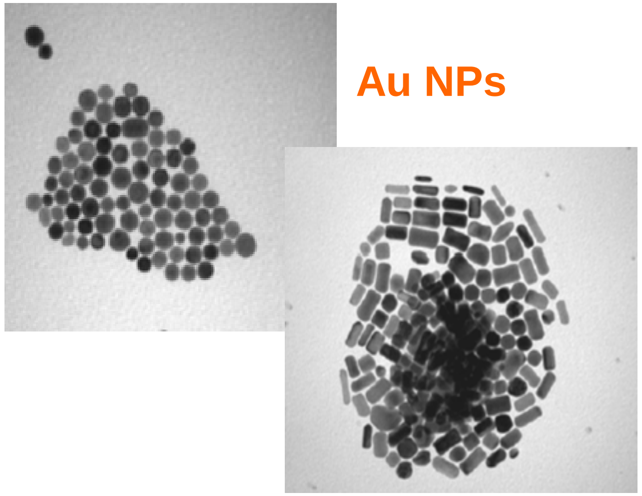
TiO_2 NCs



TiO_2-Au NPs



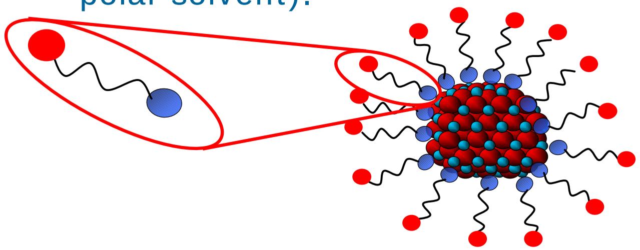
Au NPs



NC incorporation procedures

Capping exchange on surface of NCs performed to

- obtain solubility in polar solvents
- investigate the role played by surface ligands in the nanocomposite



chemical function with a high affinity to surface of NCs (thiol, amine).

group transferring the desired property to NCs (carboxylate or amine groups for NCs soluble in more polar solvent).

Functionalised NCs

Two incorporation approaches:

- Control surface chemistry by changing ligand molecules as capping layer to make NCs compatible with the desired environment
- Exploit chemical interaction between functional groups at polymer chains and ligand molecule at NC surface.

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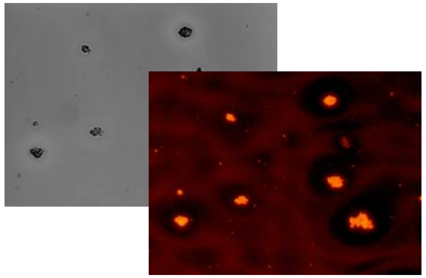
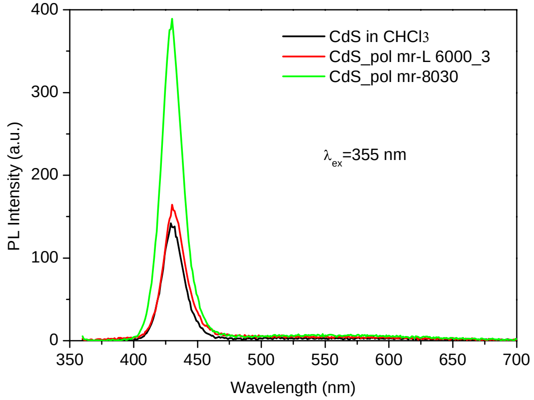
Nanocrystal modification of:

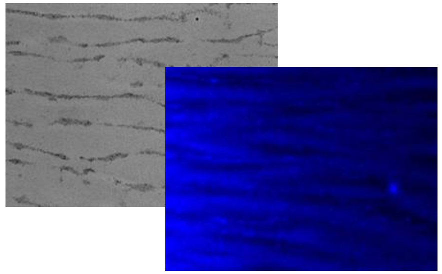
CdSe@ZnS

- **mr-I 8030 thermoplastic polymer**

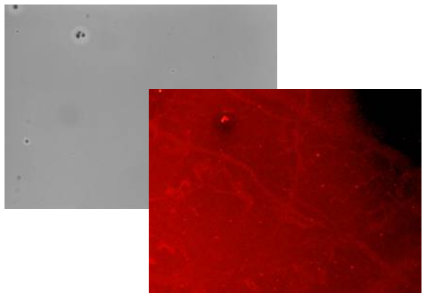
CdS

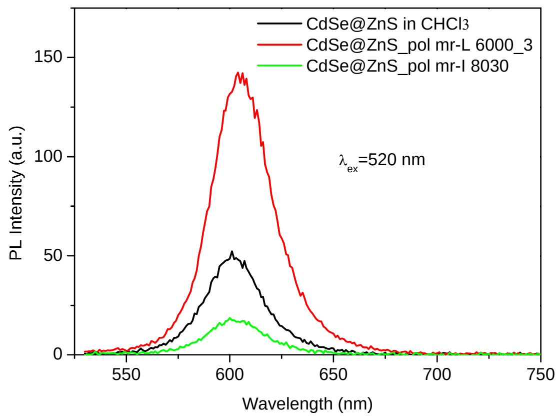


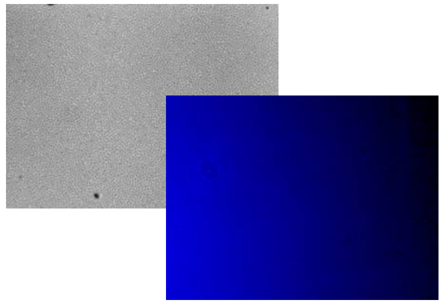




- **mr-L 6000.3 XP curing polymer**







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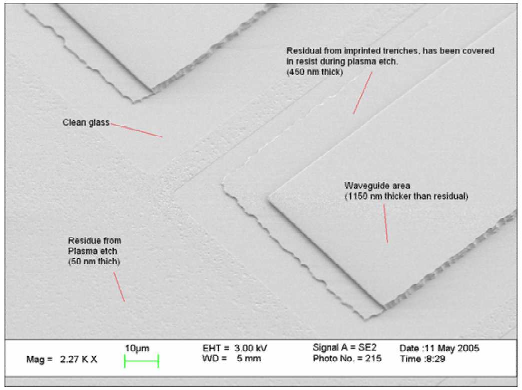
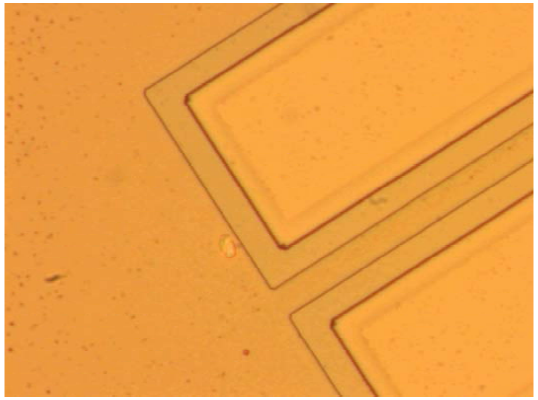
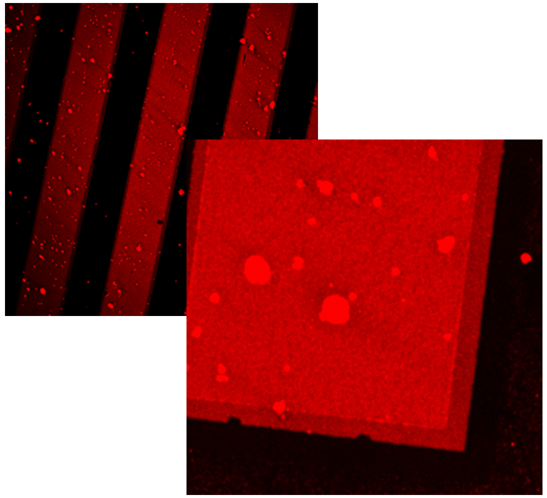
First imprinting test on NC-polymer nanocomposites

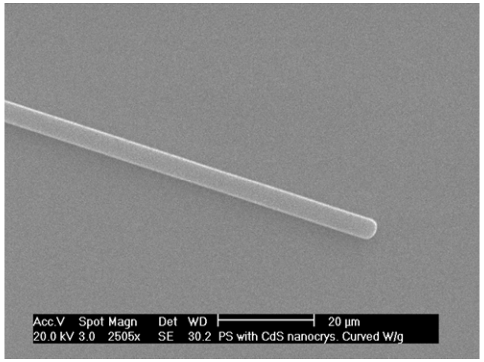
TOPAS





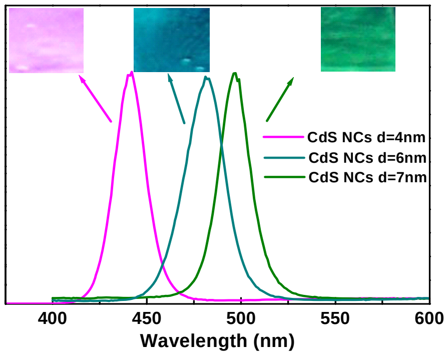


CdSe@ZnS NCs in TOPAS: imprinted laser ridges (*in collaboration with MIC*)



PS

CdS NCs in Polystyrene: imprinted waveguide (*in collaboration with Tyndall*)



PMMA

Luminescent CdS NCs in PMMA

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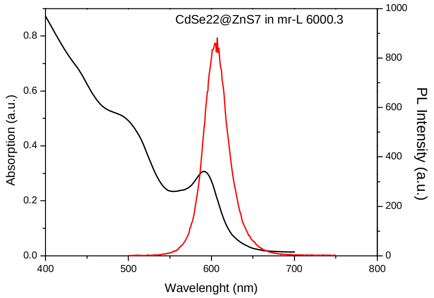
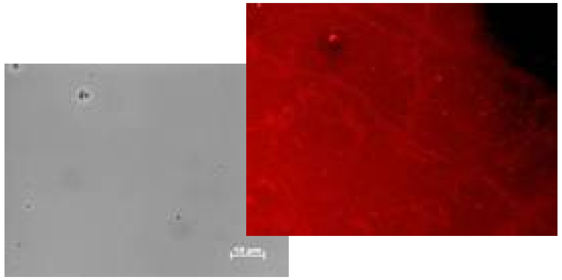
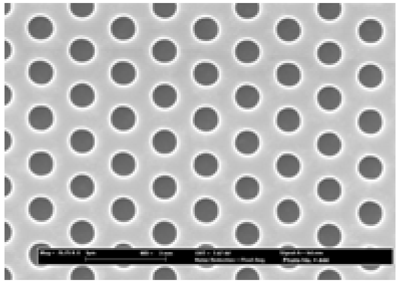
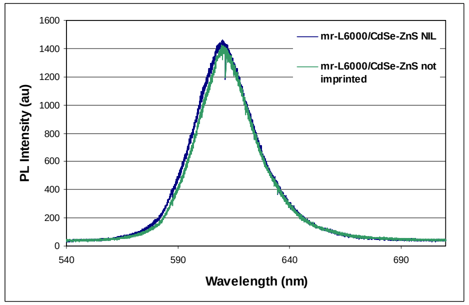
Photonic band gap structures with NC/polymer nanocomposites

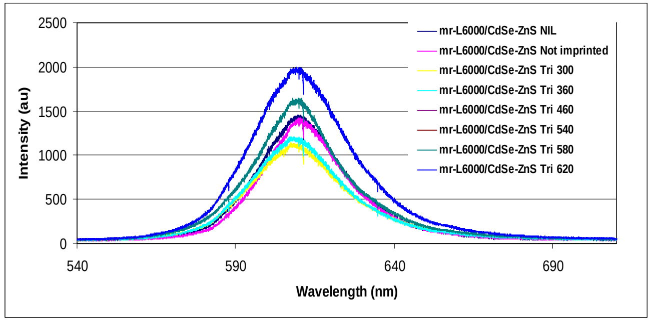
- **Slight enhancement in PL QY forCdSe@ZnS NCs in mr-L 6000.3**
  → Result of chemical interaction between polymer chains and NC surface











Optical properties of the NCs were minimally affected by the nanoimprint process

Depending on the lattice dimensions enhancement in the PL intensity up to a factor two with respect to that of the nanoimprinted unpatterned substrate

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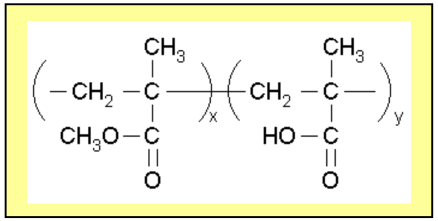
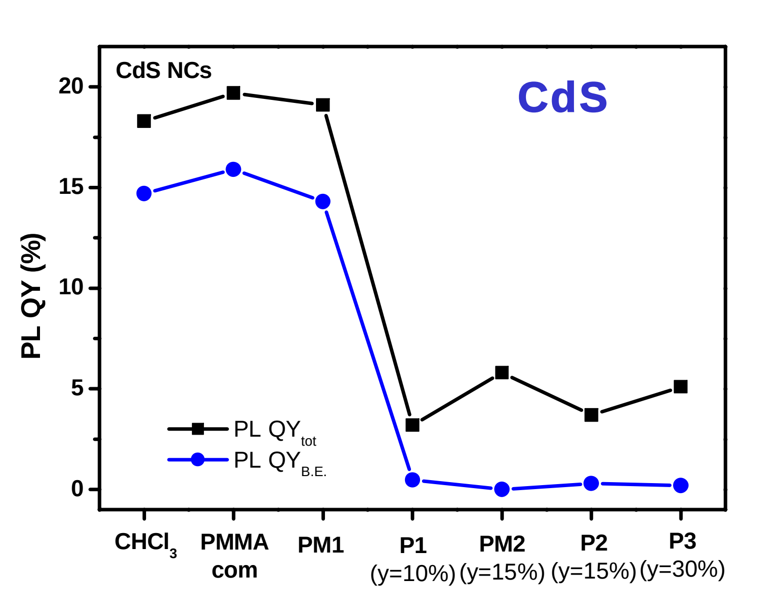
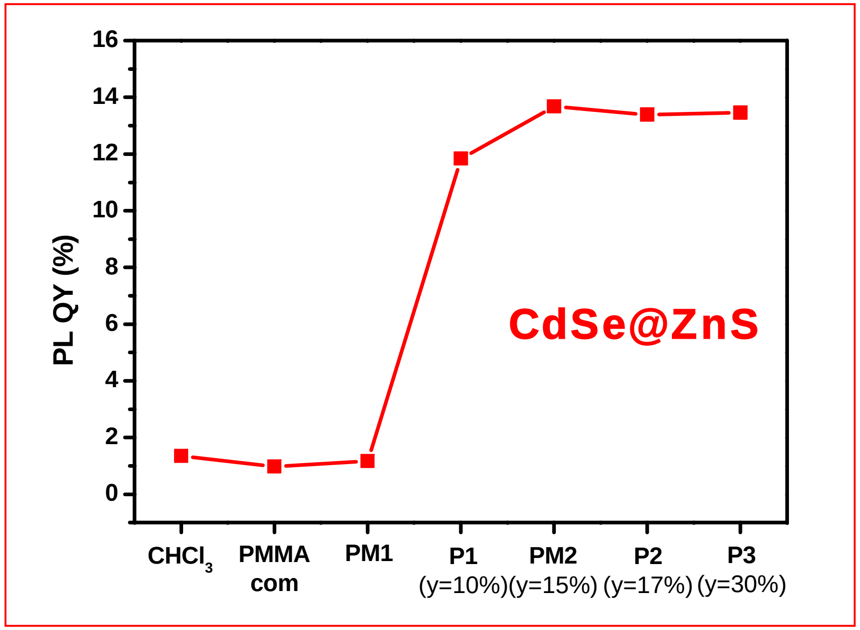
Nanocrystals in MMA-MA copolymers

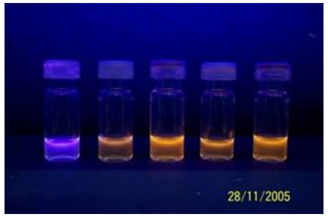


Luminescence quantum efficiency (PL QE) is highly enhanced





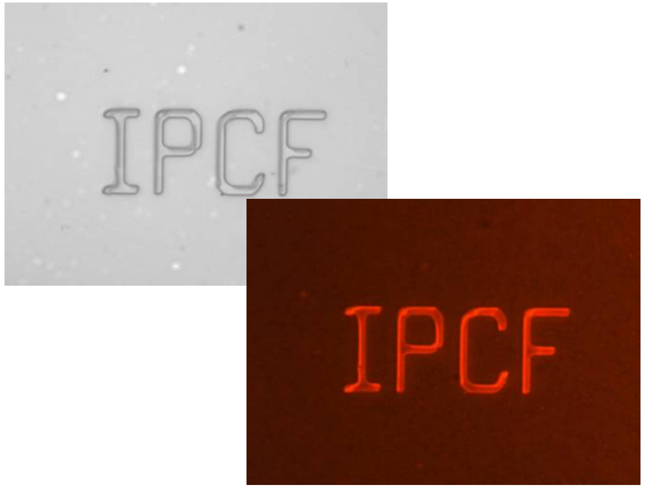
PL QY dramatically decreased

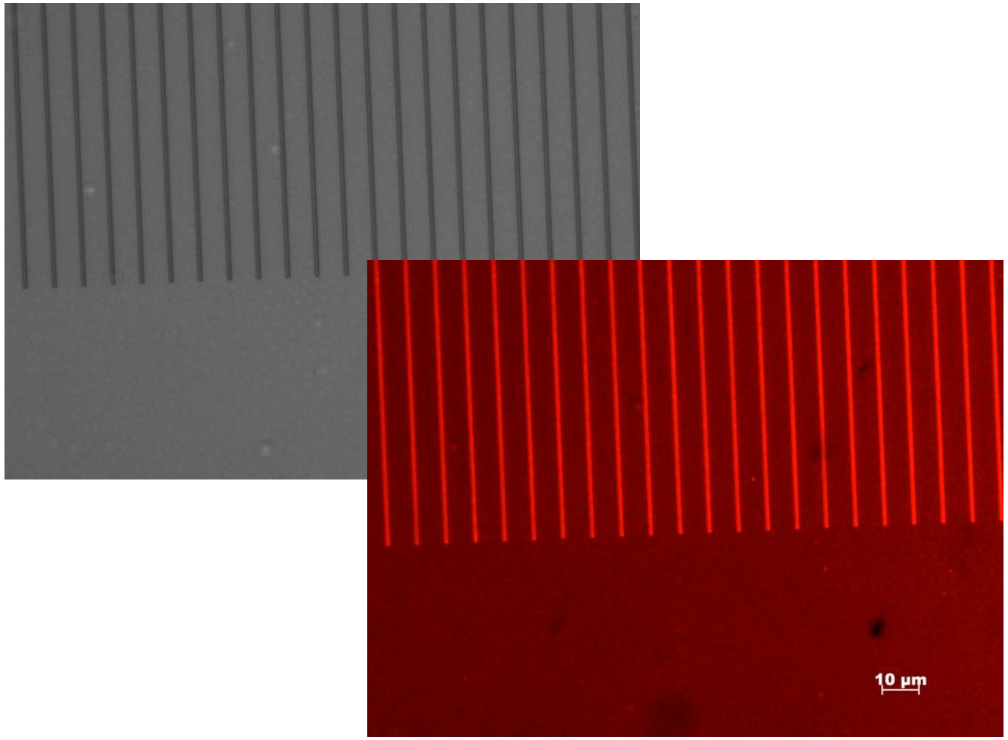


Specific interaction between the NC surface and the functional groups

Materials Subproject

Imprinting test on luminescent NCs/PMMA based co-polymer composites





Homogeneous distribution of NCs inside the polymer matrix

CdSe@ZnS NCs in PMMA modified co-polymer: imprinted waveguide
(*in collaboration with Tyndall*)

Materials Subproject

Surface modification of selected polymers by plasma treatment

OBJECTIVE

- **to improve the release process by plasma functionalisation of the polymer surface**
- in order to avoid the problems of adhesion between the stamp and the substrate during de-moulding in the NIL process

Plasma treatment of

- **polymers to be imprinted**
- **polymer stamps**

Selected polymers and surface characterization

RF and micro wave plasma
treatment of selected polymers

mr-I 7000
mr-I 8000
mr-I 9000
mr-L 6000
TOPAS
PMMA

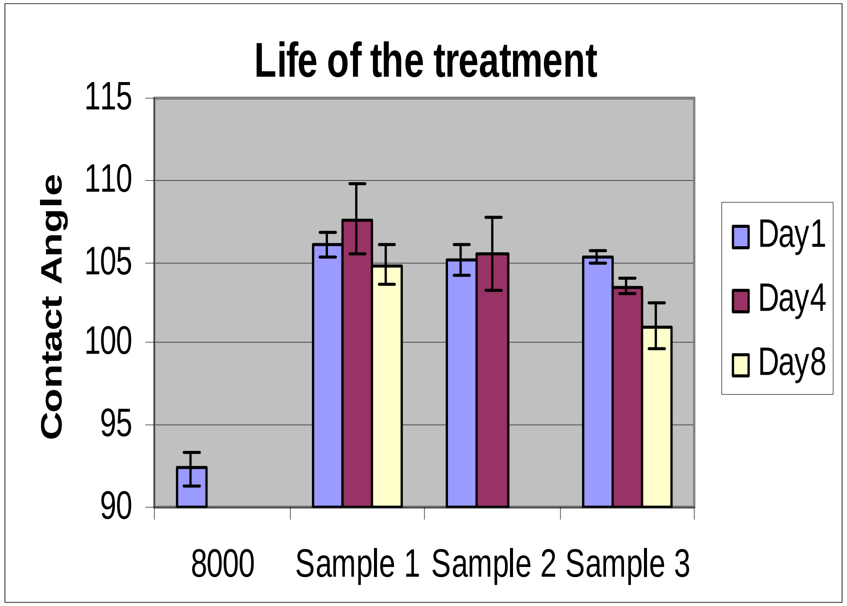
Surface characterization

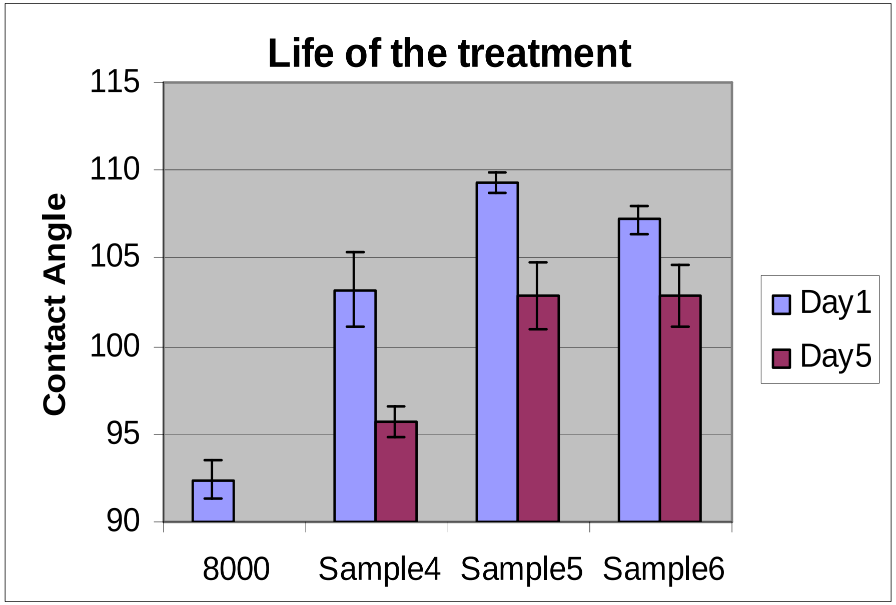
- Contact angle (DIGIDROP)
- AFM – Roughness, thickness and nanoindentation
- UFM
- XPS
- FTIR and Raman spectroscopy
- X-Ray Diffraction

Imprint tests at *PSI (Switzerland) and Tekniker (Spain)*

Materials Subproject

Durability of RF plasma treatment on mr-I 8000





Sample1 Time=2min Power=100W SF6=37,5 Ar =150

Sample2 Time=2min Power=25W SF6=50 Ar =200

Sample3 Time=2min Power=100W SfF6=200 Ar =0

Sample4 Time=1min Power=125W SF6=37,5 Ar= 100

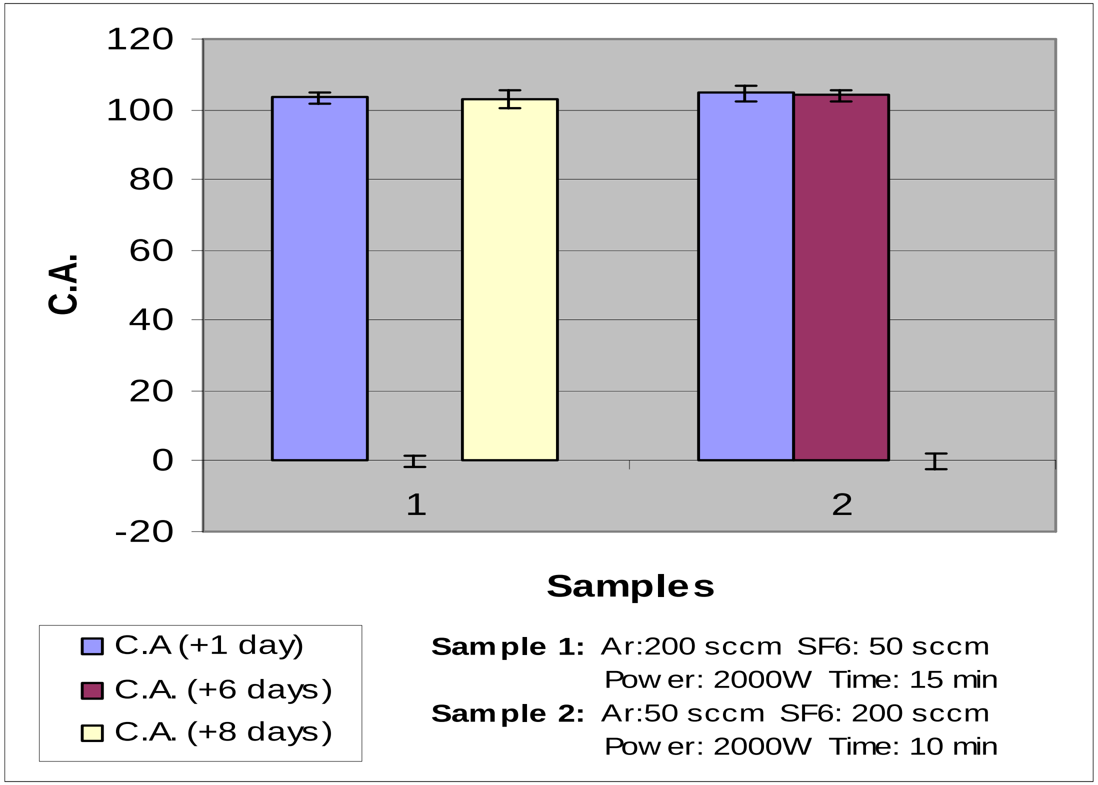
Sample5 Time=1min Power=125W SF6=175 Ar=25

Sample6 Time=1min Power=125W SF6=225 Ar= 25

Increase in contact angle from about 92° up to 108°
Under specific conditions: Decrease in contact angle up to 4° after 8 days

Materials Subproject

Durability of micro wave plasma treatment on mr-I 8000



Under specific conditions: Decrease in contact angle below 4° after 8 days

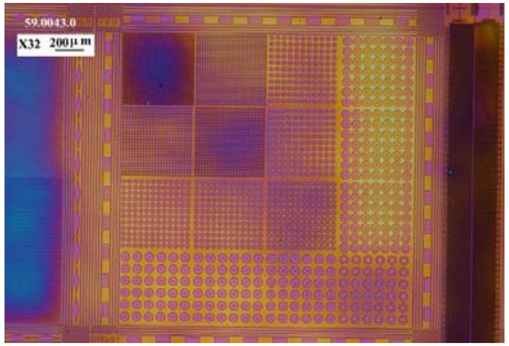
Imprint tests with plasma modified polymers

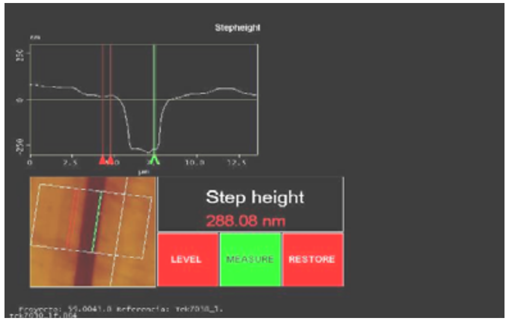
mr-I 7000
SF_6 + Ar
Microwave plasma
3000 W
10 min

⇨ Similar cavity filling and residual layer

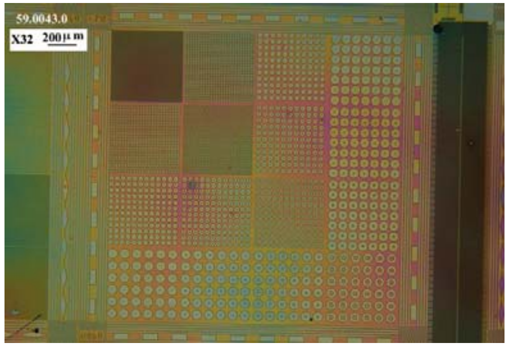
⇨ Lower surface roughness on modified surfaces

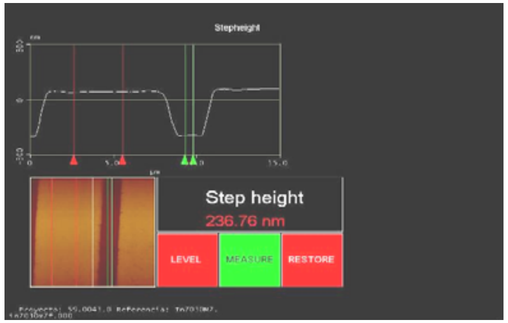
Unmodified surface





Plasma modified surface





Plasma treatment improves quality of the patterned surface

Polymer development for NIL - Strategies

Polymers for nanoimprint lithography

Curing polymers with high thermal stability

High thermal stability → plastic stamps

Materials Subproject

Polymers with low T_g

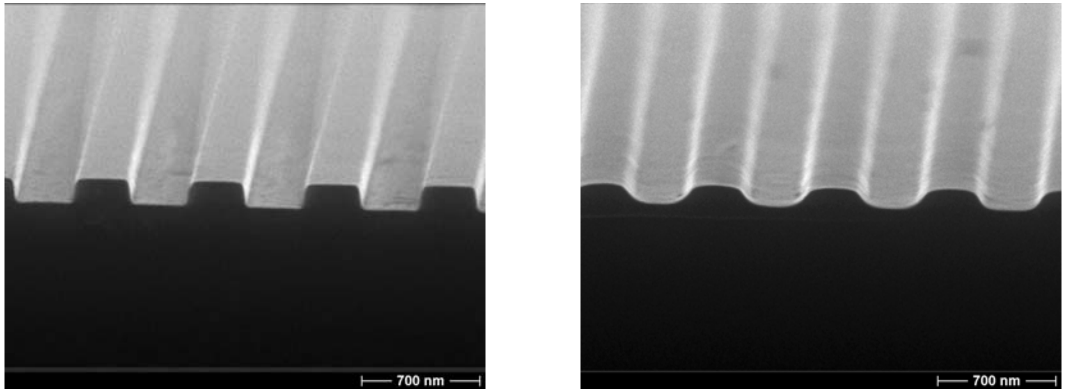
Frequent requests for polymers with low glass transition temperature

- Low *imprint temperature*
- Good *polymer flow* at moderate temperature
- Less problems with *thermal expansion*

- *Shorter cycle time* due to faster reaching the imprint temperature?
  No!
  At least with imprinters with passive cooling distinct increase in cooling time when the imprint chuck approaches ambient temperature

Thermal behaviour of thermoplastics

Example: Thermoplastic with T_g 40 °C

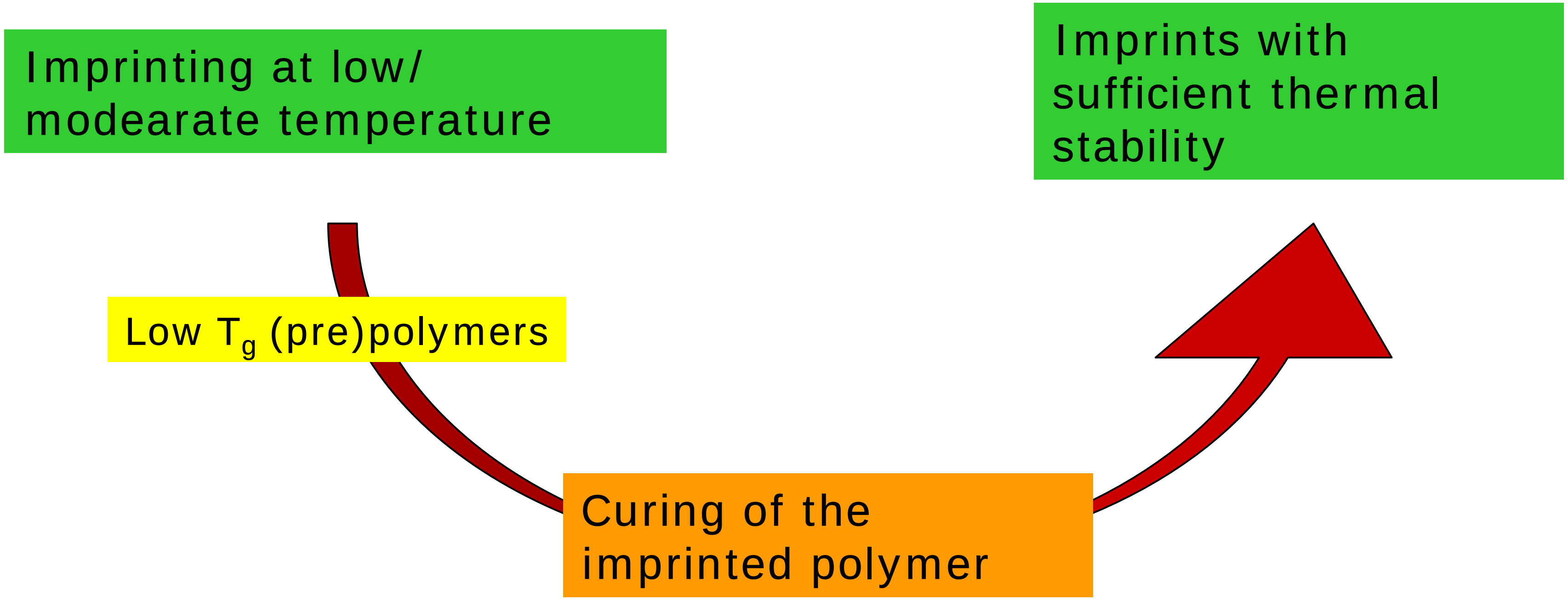


400 nm lines and trenches of the thermoplastic:
immediately after imprinting (left),
same patterns after heating the imprint to 60 °C for 5 min (right)

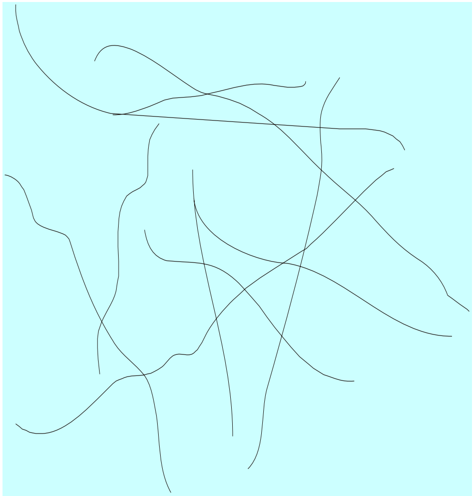
Thermal stability of imprinted patterns (deterioration by thermal flow) is determined by the glass transition temperature.

You need sufficient thermal stability of imprinted patterns in subsequent processes such as plasma etchning.

Approach to thermal stability



Thermal and photochemical curing



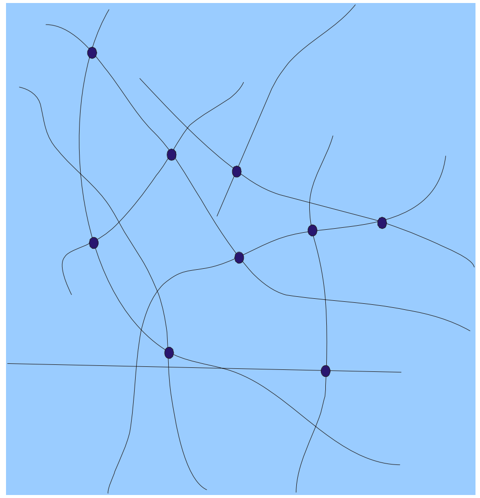
linear or branched
thermoplastic
(pre)polymer

thermal initiation

free-radical polymerization

photochemical initiation

ionic or free-radical polymerization

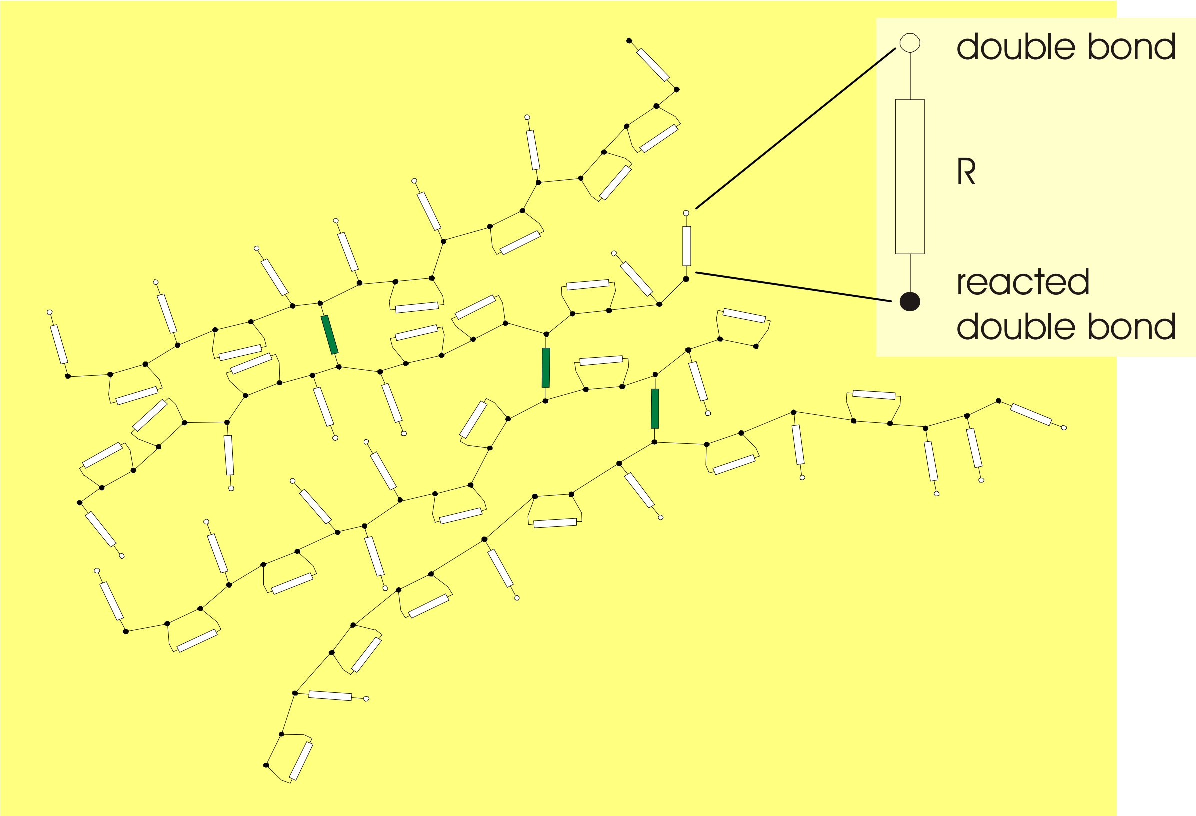


cured polymer

(Curing:
Crosslinking of the macromolecules,
generation of a spatial macromolecular network)

Materials Subproject

Schematic structure of thermally curing prepolymers



n (prepolymer) $\xrightarrow{+\,T}$ crosslinked polymer

Thermally curing polymer system

Prepolymer

Free-radical initiator

Plasticizer

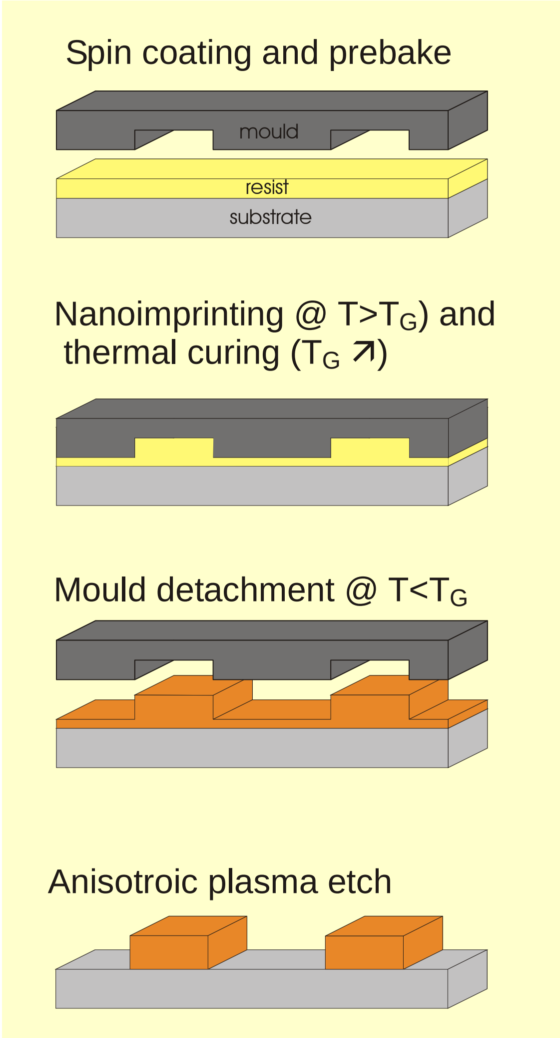
Film forming component
To build the spatial network

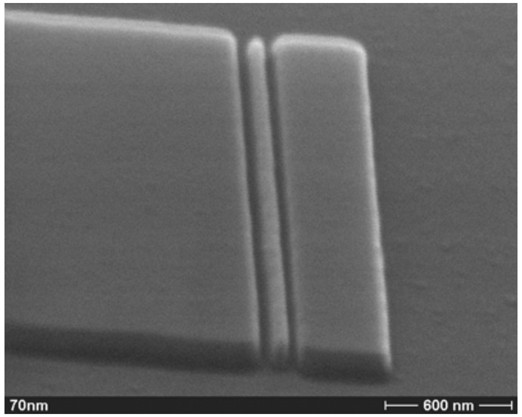
To increase curing rate (decrease curing time)
To decrease curing temperature

To allow polymer flow at lower temperature

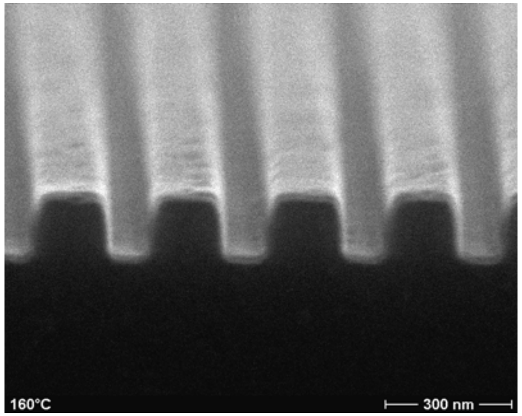
Affects flow behaviour and final thermal properties

Imprinting thermally curing polymer mr-I 9000E





50 nm line and trenches

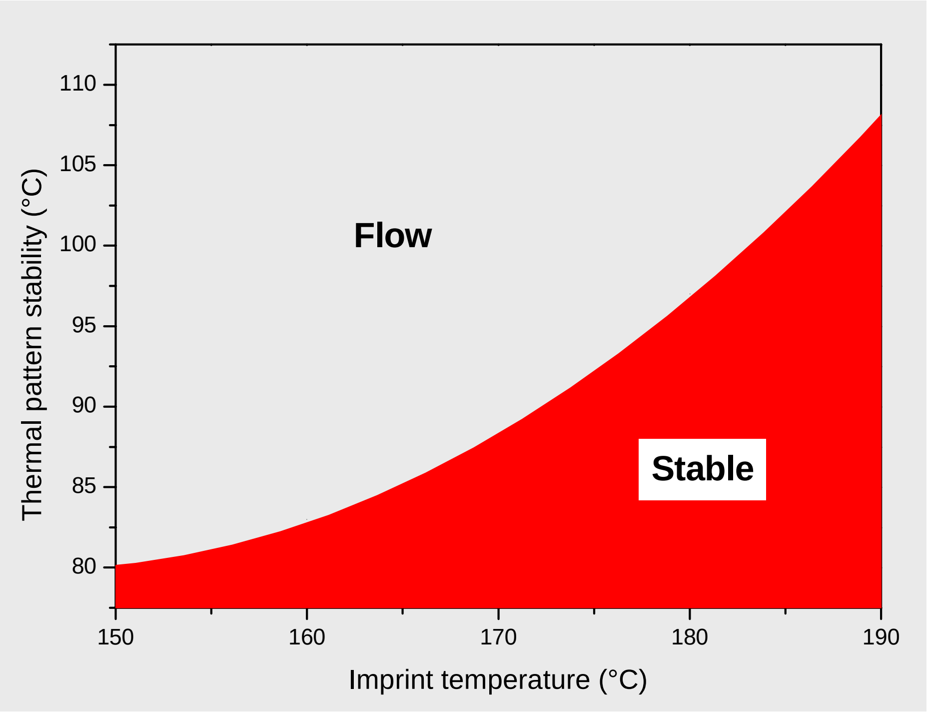


100 nm trenches

Increase in T_g during imprinting

- Thermally curing polymer system is cured during imprinting
- T_g of the imprints (→ thermal stability) of the imprints **controlled by process conditions**
  - imprint temperature
  - imprint time

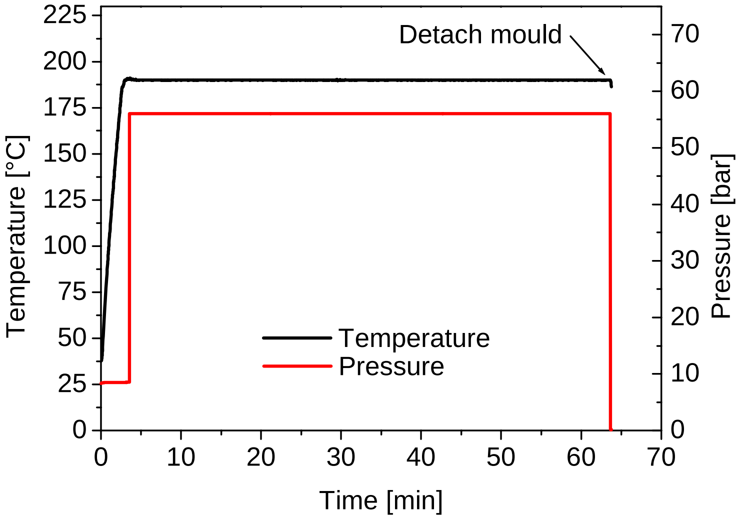
Thermal stability of imprinted patterns determined as onset of pattern flow



Imprint time 5 min
Imprint pressure 50 bar

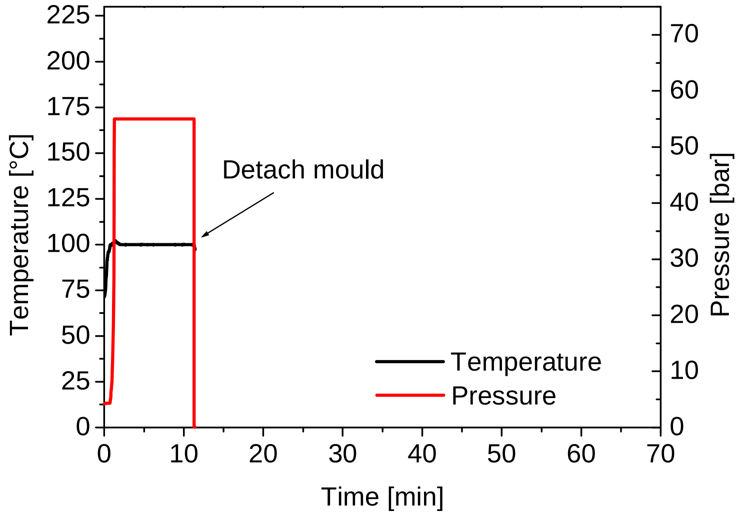
Materials Subproject

Imprinting schemes



Starting model system

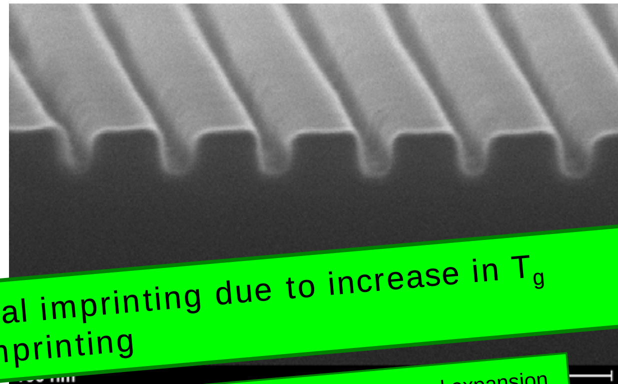
- Best imprint results (no displacement of the patterns), when **stamp is detached at imprint temperature**
- **190 °C** and **1 h** imprint time (→ sufficient curing) necessary for excellent patterns



Initiator A + Plasticizer 1

- Imprinted at **100 °C** for **10 min**, no cooling phase

→ Film thickness 170 nm, 100 nm trenches, 10 – 20 nm residual layer



Isothermal imprinting due to increase in T_g during imprinting

Litho 20

Reduction of issues of thermal expansion
Decrease in imprint time

Materials Subproject

mr-NIL 6000 – Photochemically curing resist for NIL

Resist for thermal nanoimprint lithography

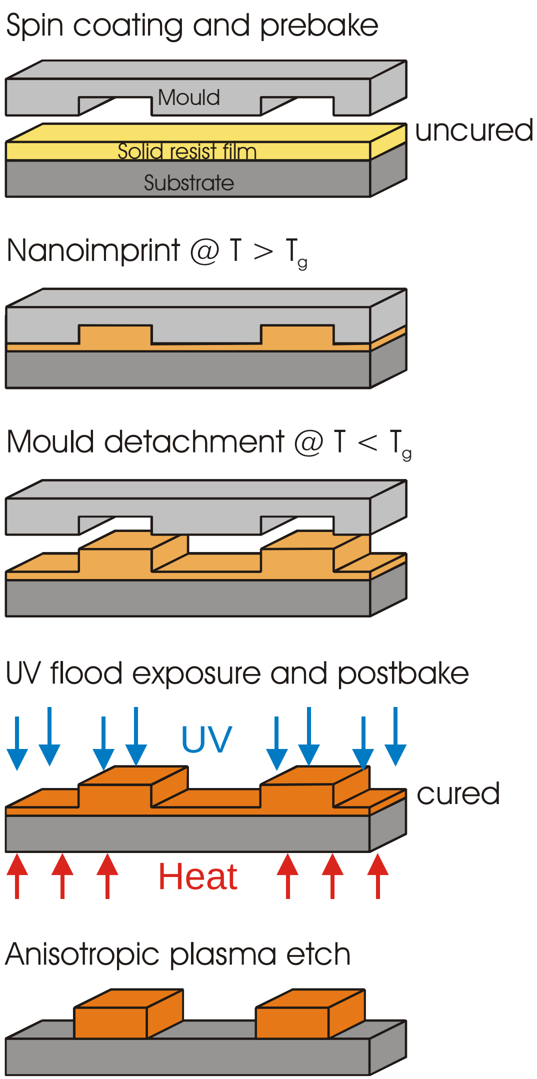
→ **solid resist film after spin coating**

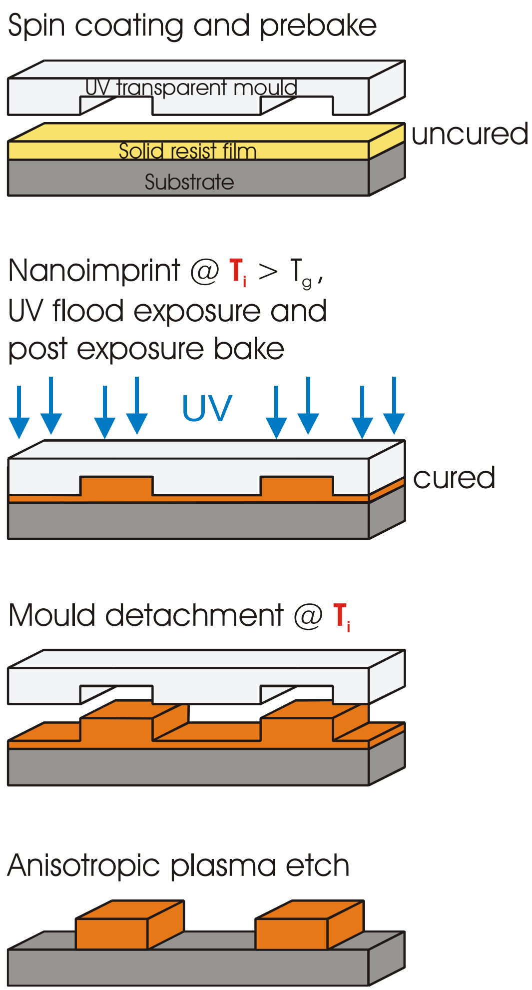
- Excellent processing, good adhesion to different substrate materials, outstanding thermal stability
- Uncured polymer: T_g = 40 °C

- Ready-to-use polymer solutions for 100, 200 and 300 nm film thickness
- Prebake 120 °C, 10 min
- Imprinting 80 – 100 °C, 30 – 60 s, 50 bar
- UV flood exposure and post bake beneficially in the imprint tool
- Resolution of at least 50 nm equidistant lines & spaces @ 300 nm film thickness
- **Plasma etch resistance** superior to PMMA
  Selectivity to SiO_2 about 2
  (CHF_3 plasma)

Materials Subproject

Process schemes



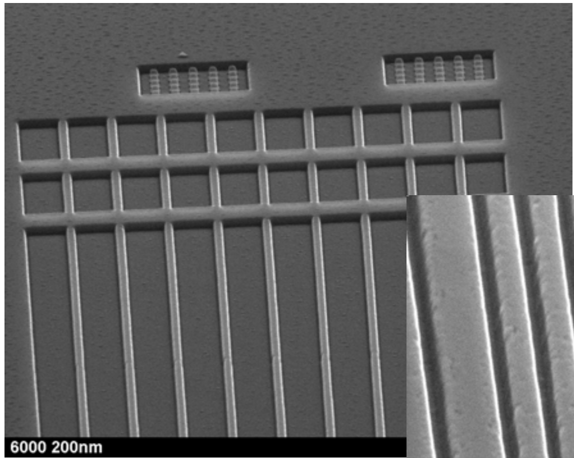


Isothermal imprinting due to increase in T_g during imprinting

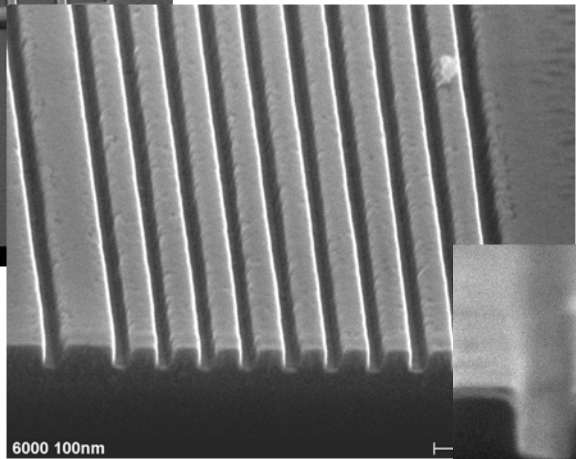
Reduction of issues of thermal expansion
Decrease in imprint time

Materials Subproject

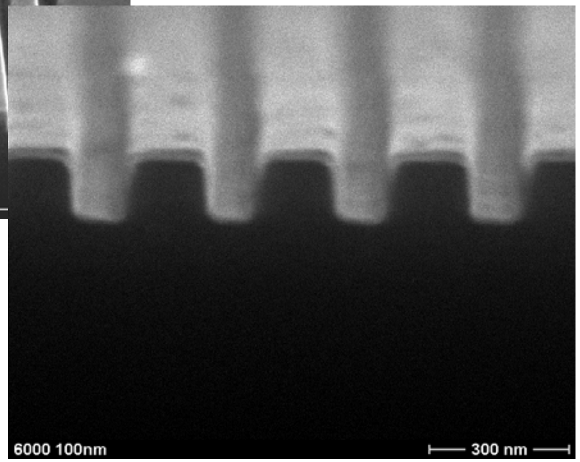
mr-NIL 6000 – Examples



200 nm patterns



100 nm trenches,
300 nm pitch



100 nm trenches,
300 nm pitch

Film thickness 300 nm

Summary

- A number of thermoplastics were developed within the NaPa project differing in thermal and other properties and functionality
- Curing polymers were developed offering the chance of isothermal imprinting
- Elaboration of surface modification of cured polymers is ongoing to to apply these polymers as working stamps for NIL.

The nanoimprint lithographer has the choice

Materials Subproject

Acknowledgements

Marion Fink, Mike Kubenz, Christine Schuster, Marko Vogler
micro resist technology GmbH Berlin

David Mecerreyes, Juan Antonio Alduncín, Jose Pomposo
Cidetec, Spain

Isabel Obieta Vilallonga, Arroyo Sainz
Inasmet, Spain

Lucia Curri, Marinella Striccoli
CNR IPCF, Italy

Nikolaos Kehagias, Vincent Reboud
Tyndall, Ireland

Anders Kristensen
MIC, Denmark

Schift Helmut
PSI, Switzerland

Cecile Gourgon, Nicolas Chaix
LTM/ CNRS, France

The presented work was partially funded by EC project NaPa (Contract no. NMP4-CT-2003-500120)