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PDMS nano-coating for glass substrates

F. Trespidi[1], G. Timò[1], F. Galeotti[2], M. Pasini[2]
[1]RSE, Piacenza, Strada torre della razza Loc. Le Mose, 29122, IT
[2]ISMAC CNR, Milano, Via E. Bassini 15, 20133, IT

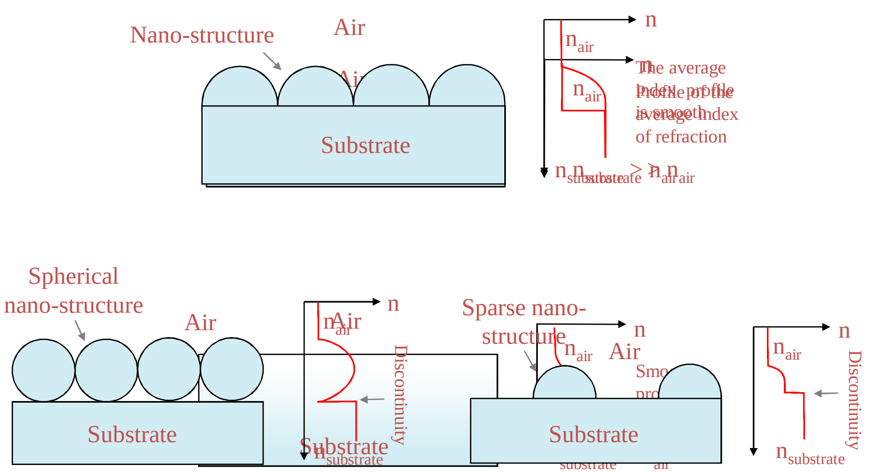
Basic idea

John William
Rayleigh
1842 – 1919

A succession of layers of material
with a gradual variation of the refractive index
show antireflection properties over a wide spectral range

(mathematically demonstrated by Lord Rayleigh
at the end of the XIX century)

Intuitive approach



Material selection

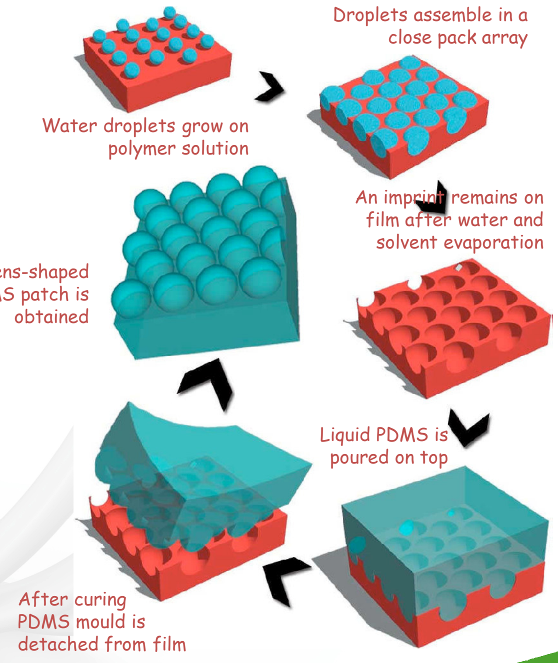
PDMS (Polydimethylsiloxane)
Cross-linked PDMS with elastomeric behaviour

Interesting properties

- transparent in the visible spectrum
- $n_{PDMS} \approx n_{glass}$
- non-hygroscopic
- good adhesion on glass
- very low cost
- inert and non-toxic
- non-flammable
- light and easily disposable

Manufacturing process

(self assembly technique by ISMAC-CNR)



Manufacturing process

Originally developed for another application:

Microsized-coating used
to increase the roughness of LED surface
thus increasing the efficiency of light extraction

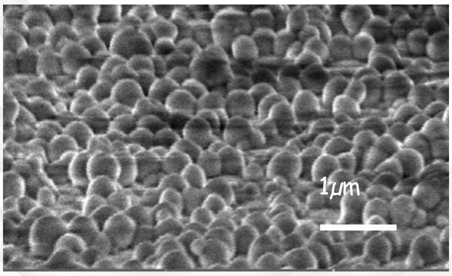
For more details on the technique:

"Breath figures-mediated microprinting allows for versatile applications in molecular biology"

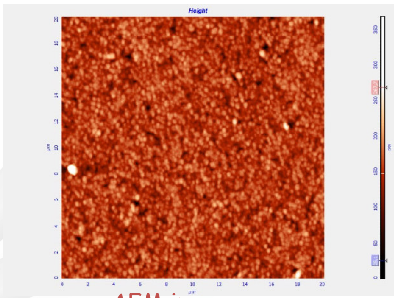
European Polymer Journal 45 (2009) 3027-3034

Nano-coating features

Coating surface
- Monolayer
- Similar to an hemispherical shape
- Size of about 300nm
- Highly packed
- Randomized distribution (avoids grating effects)

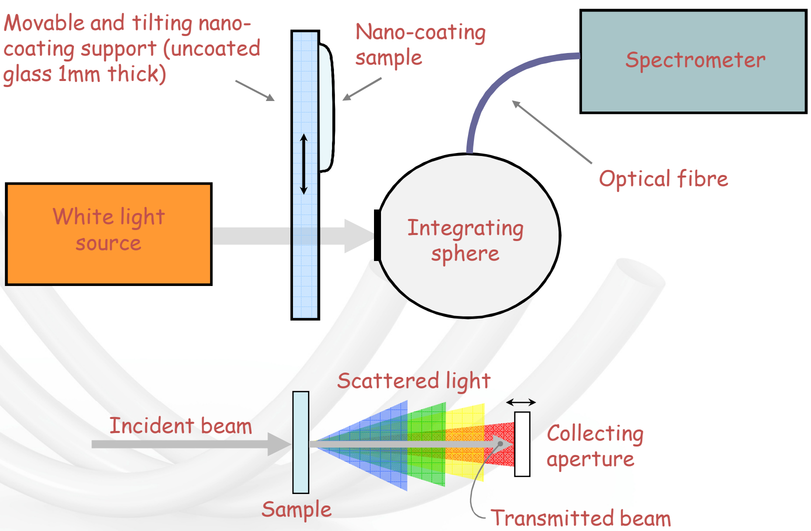


SEM image

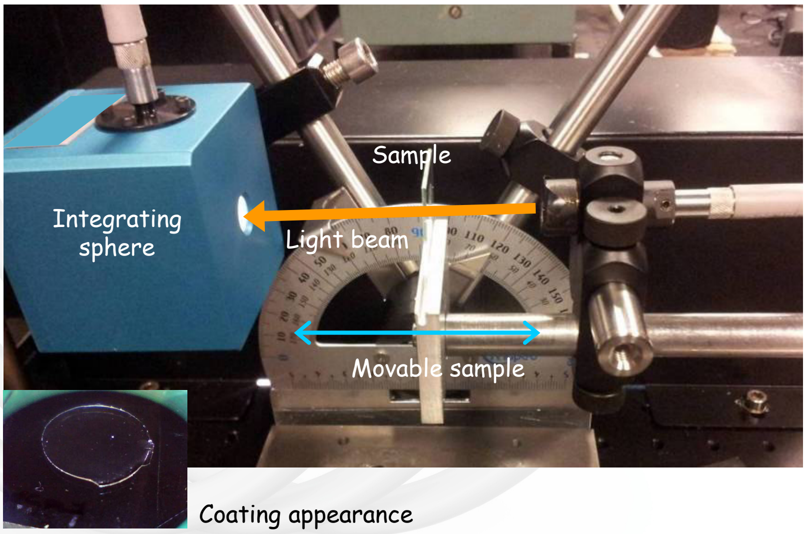


AFM image

Spectral transmission measurement

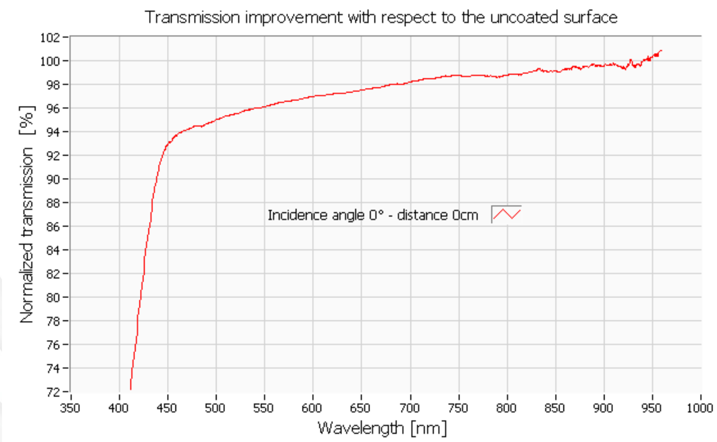


Measurement set-up



Coating appearance

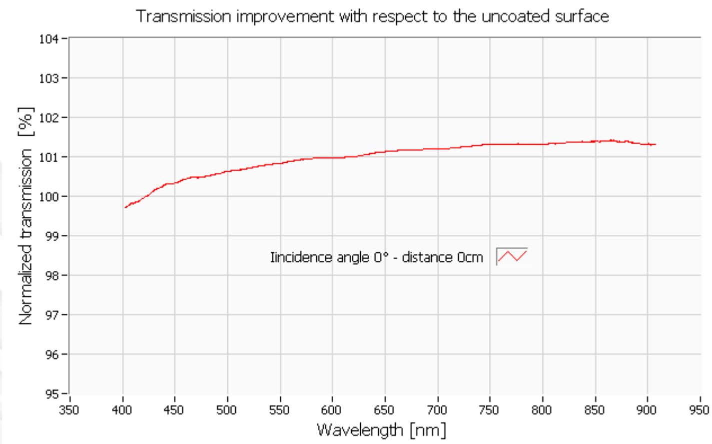
Nano-coating performances



Low-performance coating
The size of nano-hemispheres are still to large
Preliminary results are not so exciting!
but...

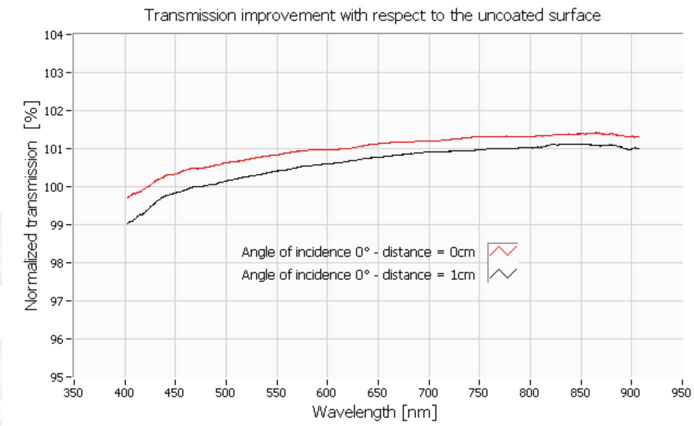
Nano-coating performances

… after optimization of the growth process for the nano-hemispheres, better results were obtained



Nano-coating performances

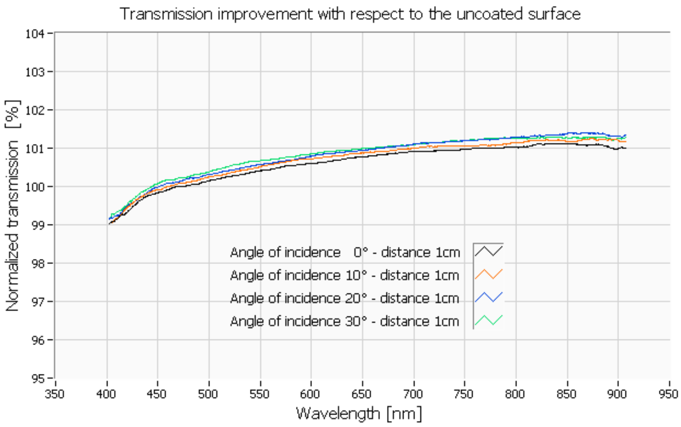
If increasing the distance between sample and collecting surface



Results are in agreement with what expected:
the transmission at shorter wavelengths decreases more rapidly

Nano-coating performances

If varying the incidence angle of the light on the sample



Performance slightly increase with the angle of incidence with respect to the uncoated glass

Future developments

- Improvement of the theoretical approach by using computer simulations (Comsol Multiphysics).
- Development of new polymers to reduce the size of the nano-structure thus improving the coating performances.
- Evaluation of ageing effects.
- Try different nano-structure geometries such as cusp (the shape complementary to the hemispheres).
- Characterization of the coating on both the glass surfaces.
- Development and testing of nano-coating for different substrates materials.

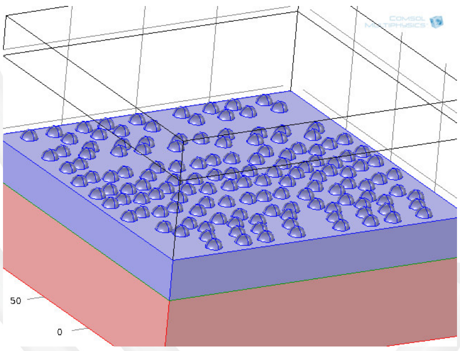
Considerations and conclusions

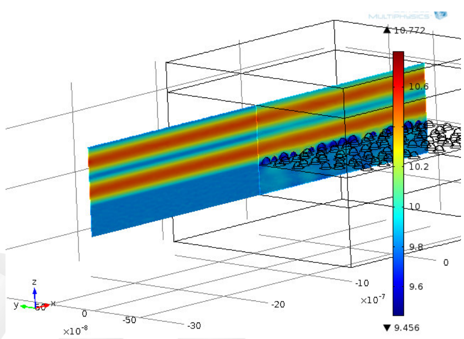
- The possibility of using nano-hemispheres of PDMS on glass surface as low cost nano-coating was demonstrated.
- An improvement in the transmission with respect to the uncoated glass was achieved in the visible and NIR ranges.
- The maximum transmission improvement of >1% was in the NIR range.
- The technique seems to be promising and further application on LED and PV systems should be investigated.

Questions?

Extra slides

Preliminary simulations





n = 2;
normal incidence;
nanoparticle diameter d = l/10

➔ Transmission improvement: +3.3%

Performed with Comsol Multiphysics

Preliminary simulations

Conditions: n= 2 , normal incidence
(no difference between TE and TM that will be present at different angle of incidence).
Nanoparticle diameter d = ι/10 (l = 500nm)
Results are the same if d/ι is maintained constant and n is the same.

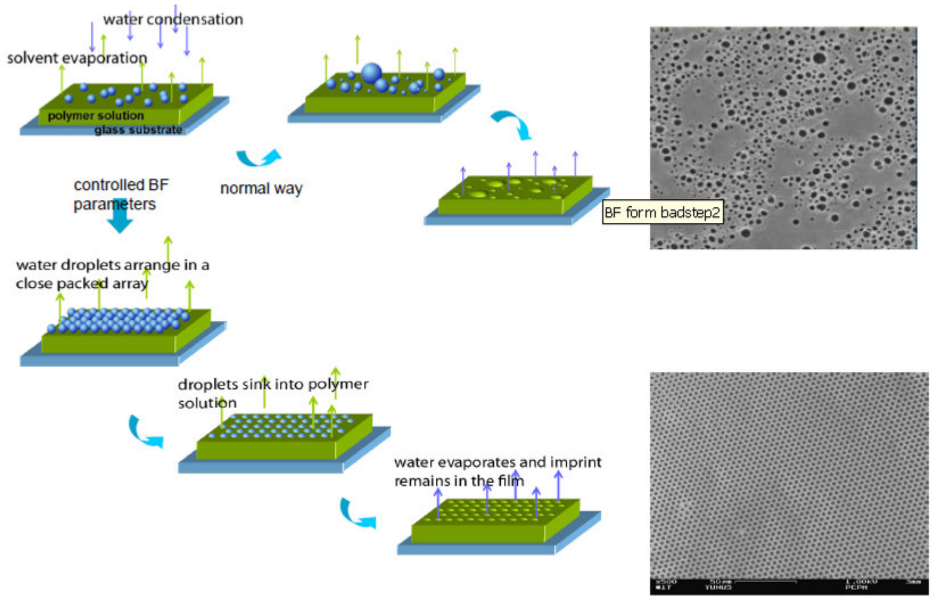
From the Fresnel equations without nanocoating the transmitted field is 8/9 while the reflected field is 1/9.

From simulation with Comsol model the found value is 0.88892 (used the S parameter) ≈ 8/9

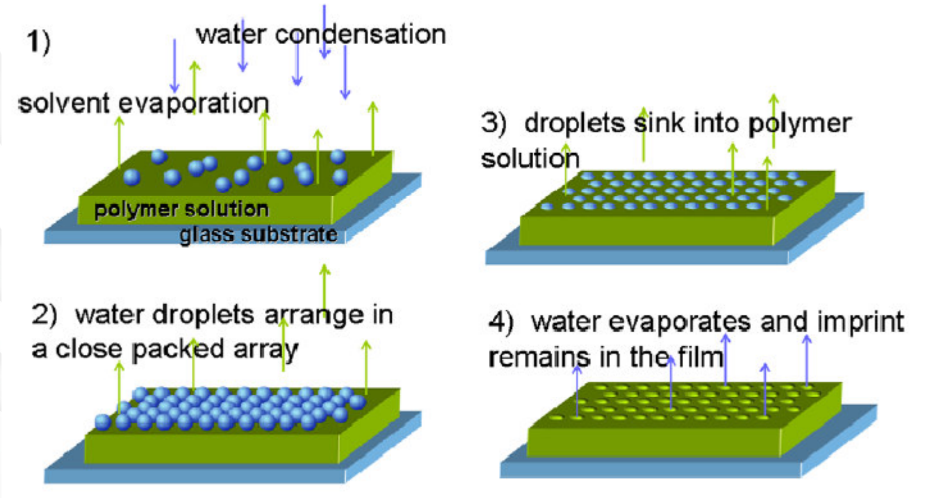
With the nano-coating: integration with the Poynting vector (less precise).

By integrating the Poynting vector: 91% without coating 94% with coating.

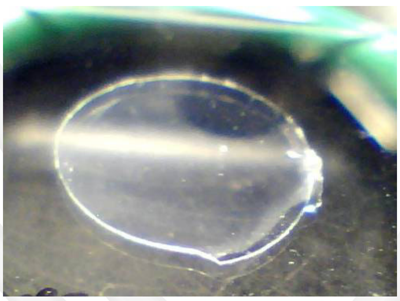
Breath figure formation



Manufacturing process



Coating appearance



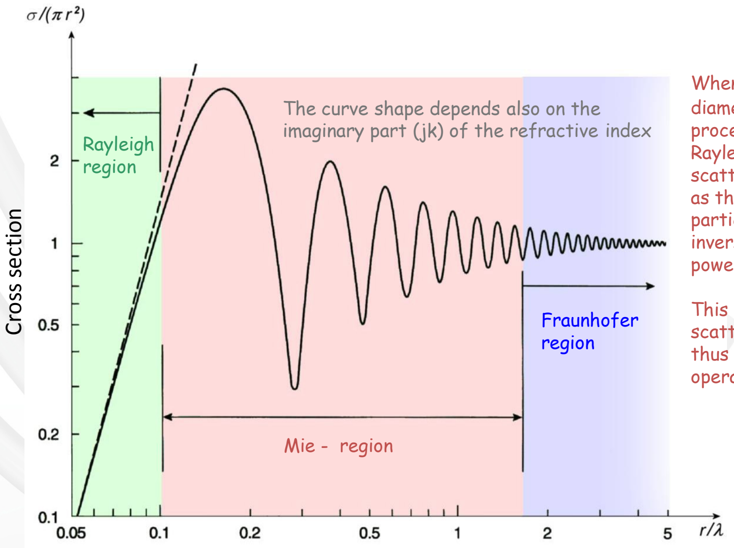
Good sample

Bad sample (milky)

Performances of the measuring instrument

Parameter	Value	Notes
Type of measure		Transmission reflection and scattering
Spectral range	400nm ÷ 900nm	Limited by the lamp spectrum and by the transmission of the optical components. The spectrometer could perform the measurements from 200nm to 1033nm.
Measurement time	1s ÷ 10s	Average integration time needed for the spectrometer measurements (depending on the coating properties).
Precision on relative measurements	≈ ±0.15%	Stability of the signal during the full measurement time by considering drift and noise from: -the spectrometer sensor; -the light source; -the background signals.
Size of the probe beam	Φ 4.5mm	Is the size of the light beam collected by the spectrometer aperture.

Scattering from a spherical particle

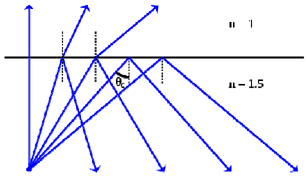


When d << λ (d = sphere diameter) the scattering process follows the Rayleigh model where the scattered power varies as the 6° power of the particle size, and inversely with the 4° power of the wavelength,

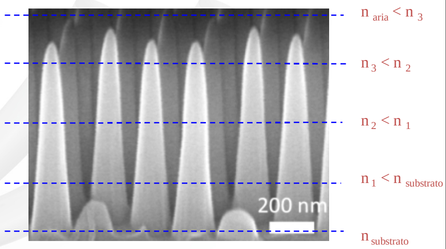
This reduces the scattered components thus allowing the operation as AR coating.

Extraction of light from LEDs: coating comparison

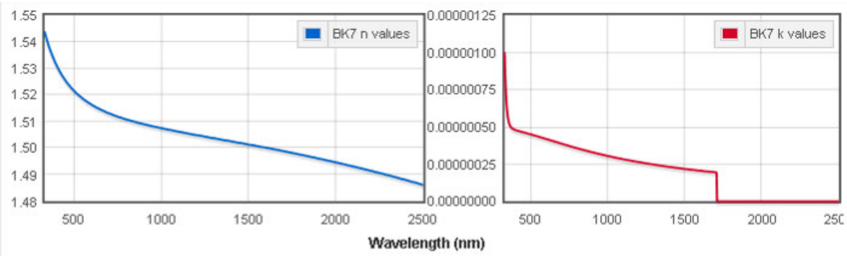
Traditional coatings ➔ Losses for:
- Total internal reflection
- Dependence on the incidence angle
- Dependence on the wavelength



Nano-structured coatings:
Creates an index matching thus reducing the reflected component.



Optical properties of BK7 glass



Refractive Index Reference - From transmittance spectrum of 200 micron thick sample

http://www.filmetrics.com/refractive-index-database/BK7/Float-Glass

Optical properties of PDMS

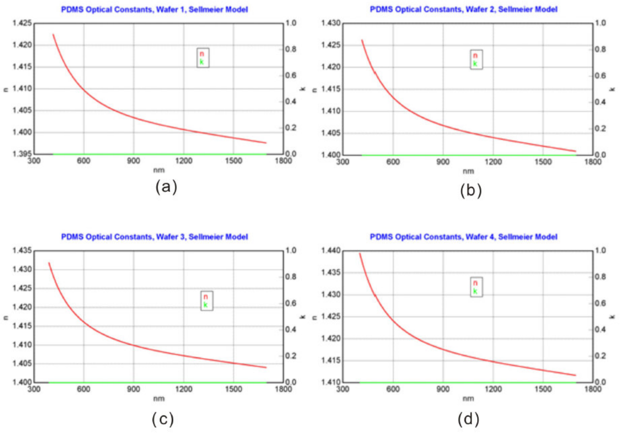


FIGURE 2.3. Refractive index for different mixing ratio of Sylgrad 184. (a) Sylgard 184(20 : 1) , (b) Sylgard 184 (10 : 1), (c) Sylgard 184(5 : 1), and (d) Sylgard 184(2.5 : 1)

From Thesis : PDMS Based Waveguides for Microfuidics and EOCB

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Physical properties of PDMS (1of2)

Property	Value	Reference	Image/URL
Mass density	0.97 kg/m^3	Polymer Data Handbook, Mark J., Oxford Univ. Press, New York (1999)	
Young's modulus	360-870 KPa	Re-configurable Fluid Circuits by PDMS Elastomer Micromachining	http://mass.micro.uiuc.edu/ publications/papers/26.pdf
Poisson ratio	0.5	Polymer Data Handbook	
Stiffness Constants			
Tensile or fracture strength	2.24 MPa	Polymer Data Handbook	
Residual stress on silicon			
Specific heat	1.46 kJ/kg K	Polymer Data Handbook	
Thermal conductivity	0.15 W/m K	Polymer Data Handbook	
Dielectric constant	2.3-2.8	Polymer Data Handbook	
Index of refraction	**1.4**	Polymer Data Handbook	
Electrical conductivity	$4x10^{13}$ Ωm	Polymer Data Handbook	
Magnetic permeability	$0.6x10^6$ cm^3/g	Polymer Data Handbook	
Piezoresistivity	N/A		
Piezoelectricity	N/A		

http://www.mit.edu/~6.777/matprops/pdms.htm

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Physical properties of PDMS (2of2)

Property	Value	Reference	Image/URL
Wet etching method	tetrabutylammonium fluoride ($C_{16}H_{36}FN$) + n-methyl-2-pyrrolidinone (C_5H_9NO) 3:1	J. Garra, T. Long, J. Currie, T. Schneider, R. White, M. Paranjape, "Dry Etching of Polydimethylsiloxane for Microfluidic Systems", Journal of	http://scitation.aip.org/journals/doc/JVTAD6-ft/vol_20/iss_3/975_1.html
Plasma etching method	CF_4+O_2	J. Garra, T. Long, J. Currie, T. Schneider, R. White, M. Paranjape, "Dry Etching of Polydimethylsiloxane for Microfluidic Systems", Journal of Vacuum Science and Technology, A20, pp 975-982, 2002.	http://scitation.aip.org/journals/doc/JVTAD6-ft/vol_20/iss_3/975_1.html
Adhesion to silicon dioxide	Excellent	Re-configurable Fluid Circuits by PDMS Elastomer Micromachining	http://mass.micro.uiuc.edu/publications/papers/26.pdf
Biocompatibility	Noniritating to skin, no adverse effect on rabbits and mice, only mild inflammatory reaction when implanted	Polymer Data Handbook; Belanger MC, Marois Y. Hemocompatibility, biocompatibility, inflammatory and in vivo studies of primary reference materials low-density polyethylene and polydimethylsiloxane: a review. J Biomed Mater Res 2001;58(5):467–77.	
Hydrophobicity	Highly hydrophobic, contact angle 90-120°	Re-configurable Fluid Circuits by PDMS Elastomer Micromachining	http://mass.micro.uiuc.edu/publications/papers/26.pdf
Melting Point	-49.9–40°	Knovel Critical Tables	

http://www.mit.edu/~6.777/matprops/pdms.htm

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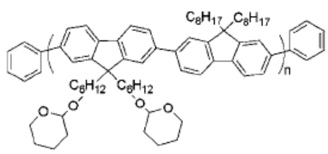
Active materials for BREATH FIGURES



Polyfluorene derivatives synthesized obtained via suzuki coupling in ISMAC Laboratory

Entry	Mn(kDa)	Mw(kDa)	Mw/Mn
Sample 07	31.7	73.4	2.32
Sample 207	25.0	71.0	2.7

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Minimum size of the nanospheres

Review article of Martina Stenzel (Journal of Polymer Science 2006)

PORE SIZE
Control over the pore size is an important factor when it comes to the preparation of honeycomb-structured, porous films for specific applications. Although pore sizes ranging around 10 lm and above might be of interest for cell patterning, small pores in the nanometer
range are desirable for photonics. The pore size is basically dictated by the size of the water droplets when they are frozen in place by the precipitating polymer at the interface during the casting process.
The smallest theoretical size of a water droplet at room temperature
has been reported to be 10 nm [1]. However, a film with pore sizes below **100 nm** has never been prepared with the breath figure technique.
The preparation of big pores is, in contrast, limited by the stability of water droplets against coagulation.

Pore size control is influenced by the nucleation and growth of droplets before encapsulation by a polymer layer occurs. The water droplet size is dictated by a wide range of variables, including the temperature of the solution, the rate of evaporation, and the precipitation of the polymer. The complexity of the process with its manifold influences does not readily allow an absolute prediction of the pore size, and current knowledge restricts us to the development of empirical relationships to permit a rough prediction capacity for governing the pore size, as given next.

[1] Kittel and Kroemer, Thermal Physics (book) 1980

(10nm would be a size well below the roughness that in general has a film obtained by the cast)