Interplay between polymers and metal oxides: the assembly of TiO_2 (nanoparticles) into mesoporous and crystalline structures

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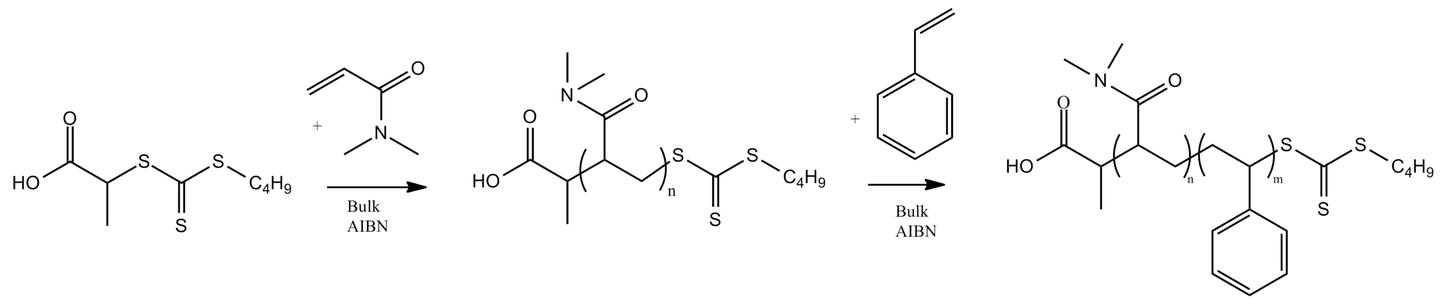
Introduction

TiO_2 can be used in many applications: (photo)catalysis, sensing, Li-ion insertion… Generally a high **crystallinity degree**, **surface area** and a control on **pore size** is needed for profoundly performing materials. We synthesized **PDMA-b-PS** block copolymers to assemble TiO_2 (nanoparticles) to mesoporous structures.

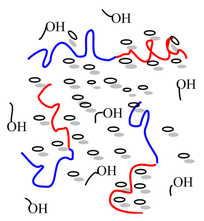
PDMA-b-PS

PDMA-b-PS (poly(dimethylacrylamide)-block-polystyrene) synthesized via RAFT-polymerization

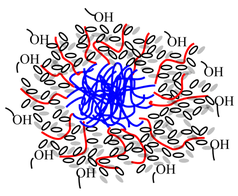


Block copolymer	*PDMA* [kDa]	*PS* [kDa]	*Đ*
$PDMA_{5k}$-b-PS_{5k}	5.1	5	1.15
$PDMA_{5k}$-b-$PS_{7.5k}$	5.1	7.5	1.16
$PDMA_{5k}$-b-PS_{8k}	5.1	8	1.14
$PDMA_{5k}$-b-PS_{9k}	5.1	9	1.26
$PDMA_{5,7k}$-b-PS_{36k}	5.7	36	1.24

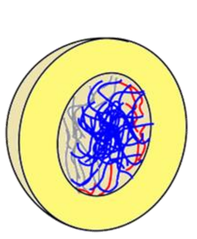
Sol – gel route



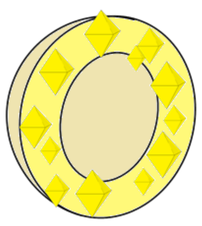
Solution
PDMA-b-PS is dissolved in THF, EtOH, HCl and Ti(IV)isopropoxide are added



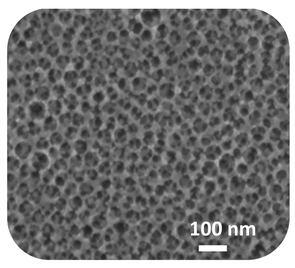
Aggregation
Reflux 1h at 45 °C, 20h at 90 °C
2d evaporation of solvents



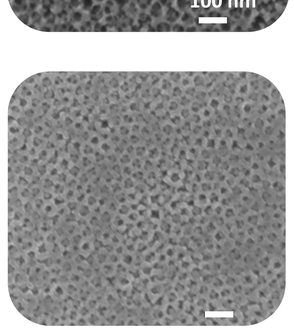
Amorphous TiO_2
2d reflux 0,1 M NaOH [1]
1h microwave treatment at 120°C [2]



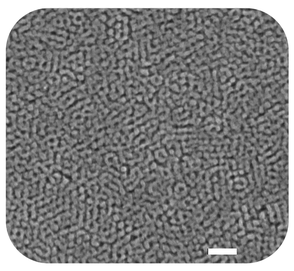
Crystalline TiO_2
2h at 450 °C, 2°C/min ramp



$PDMA_{5,7k}$-b-PS_{36k}



$PDMA_{5k}$-b-PS_{9k}



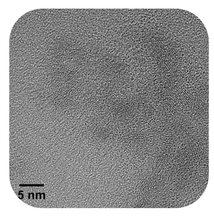
$PDMA_{5k}$-b-$PS_{7.5k}$

	Crystallinity degree (% anatase)	S_{BET} *(m²/g)*	*Pore Size (nm)*
Sol-gel route	40 – 60 %	240 - 310	7 - 40

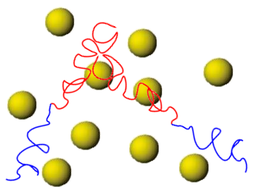
1 Meynen V., et al., *Microporous and Mesoporous Materials*, **125**, 2009.
2 Meire M., et al., *Journal of Material Science*, **51**, 2016.

Nanocrystal route

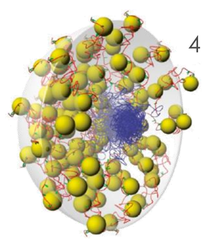
Nanocrystal (NC) synthesis
$TiCl_4$, toluene, t-BuOH are heated 2 x (90°C(1min) – 50°C (20min)) in microwave [3]



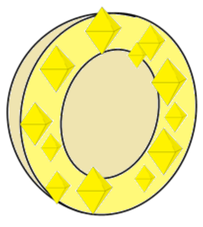
Suspension
NP's in EtOH are added to PDMA-b-PS solution in THF



Aggregation
3d evaporation of solvents



Crystalline TiO_2
2h at 400 °C, 2°C/min ramp



	Crystallinity degree (% anatase)	S_{BET} *(m²/g)*	*Pore Size (nm)*
NC route	75 – 85 %	250 - 280	7 - 40

3 Szeifert J.M., et al., *Journal of the American Chemical Society*, **132**, 2010.
4 Buonsanti R., et al., *Nano letters*, **12**, 2012.

Application

Large pores: easily accessible
Li-ion batteries: 30 – 50 nm
Photo catalysis: 10 nm
F.e. degradation Moxifloxacine

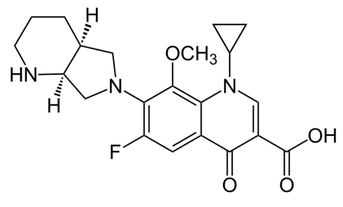
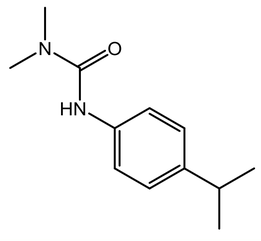
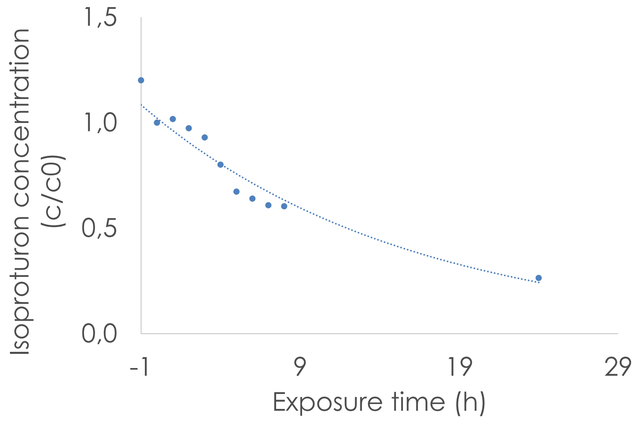


Photo catalysis: degradation **Isoproturon**
With TiO_2 ($PDMA_{5k}$-b-PS_{9k}), sol-gel method, 60 % anatase, 240 m²/g

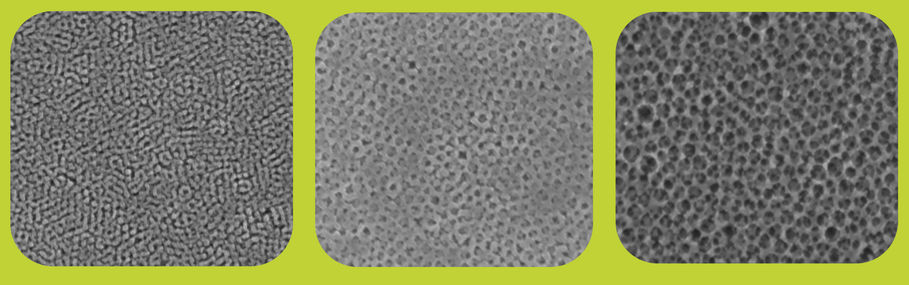




Conclusion

By using self-synthesized PDMA-b-PS we were able to make mesoporous and crystalline TiO_2 with:

Control on **pore size**: 7 – 40 nm
Surface area: S_{BET} 240 – 310 m²/g
Crystallinity degree: 40 – 85 %anatase



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