# Ordering of $TiO_2$ nanoparticles to mesoporous structures using self-synthesized acrylamide-styrene block copolymers

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## Introduction

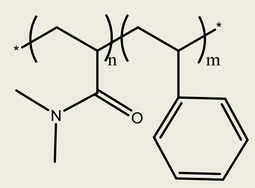
**Mesoporous, crystalline metal oxides** are rapidly gaining importance for applications in sensors, (photo)catalysis and energy generation/storage. For most applications, the ideal material should be **crystalline** as well as **porous**, enhancing surface related phenomena. The commonly used synthetic procedures involve the creation of an amorphous network from sol-gel precursors templated by organic surfactants. This requires crystallization at elevated temperatures, which often results in a collapse of the mesostructure, because the surfactant generally degrades before $TiO_2$ crystallization. Hence, specific surfaces > 250 $m^2/g$ are only reported for largely inefficient amorphous materials processed at reduced temperatures.(1)

**Two approaches** will be investigated to tackle the trade-off between crystallinity and increased surface. The first encompasses the application **thermally stable block copolymers**, used as pore formers, suppressing shrinkage and collapse of the mesoporous structure during crystallization at elevated. With this sol-gel approach a **surfactant** is mixed with a **$Ti^{4+}$- precursor** (Ti-isopropoxide and HCl) that hydrolyses and condenses around the supramolecular structure formed by the surfactant. In a next step the surfactant is removed by a **thermal procedure** which also **crystallizes the titania** (+ 400 °C). The second strategy consists of the **ordering of previously synthesized nanocrystals to porous structures**. Here **nanocrystals** are ordered into a porous structure with **suitable surfactant molecules**. This will lead to an important reduction of the processing temperatures: a **mild temperature treatment** is sufficient **to connect the particles** and remove the template. For the two approaches the $TiO_2$ powders are formed via EISA (Evaporation Induced Self-Assembly) at 60°C. Finally, a thermal treatment is performed: 2h at 450 °C, 2°C/min.

## Block copolymer

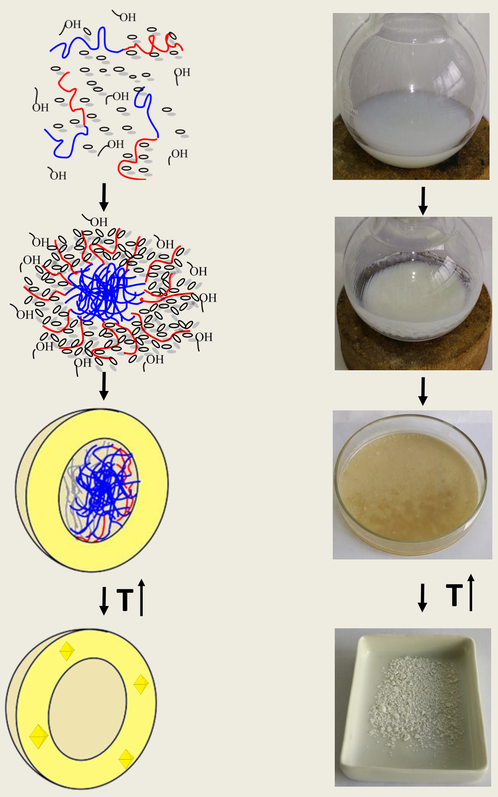
PDMA-b-PS (Poly(dimethylacrylamide)-block-polystyrene):

- Via Reversible Addition Fragmentation chainTransfer (RAFT)

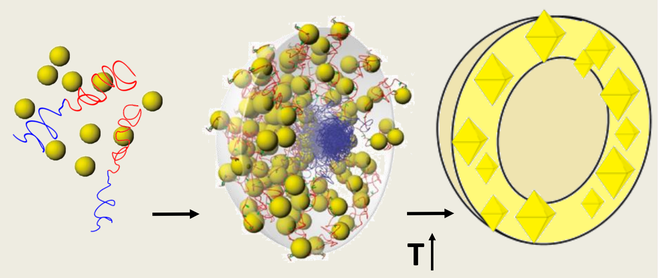



| Polymer | PDMA (g/mol) | PS (g/mol) | PDI |
|---|---|---|---|
| PDMA-$PS_{4k}$ | 5000 | 4000 | 1.2 |
| PDMA-$PS_{5k}$ | 5000 | 5000 | 1.26 |
| PDMA-$PS_{7,5k}$ | 5000 | 7500 | 1.16 |
| PDMA-$PS_{9k}$ | 5000 | 9000 | 1.18 |

## Sol-gel approach

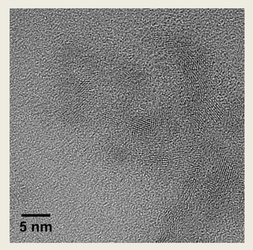


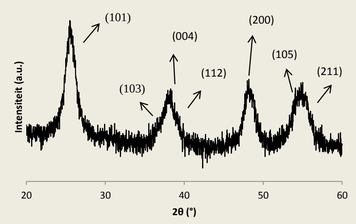

## Nanocrystal soft-templating approach



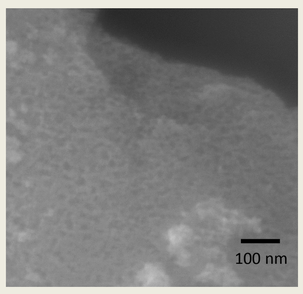

Ultrasmall spherical nanoparticles are used:

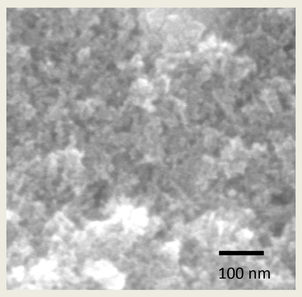
- Microwave synthesis with *tert*-BuOH, toluene and $TiCl_4$ (2)
- Suspendable in EtOH




## Porous and crystalline powders




| Sol-gel approach: BET surface area ($m^2/g$) | Polymer | Nanocrystal approach: BET surface area ($m^2/g$) |
|---|---|---|
| 241 | PDMA-$PS_{4k}$ | 270 |
| 211 | PDMA-$PS_{5k}$ | / |
| 192 | PDMA-$PS_{7,5k}$ | (97) |
| 215 | PDMA-$PS_{9k}$ | (88) |

## Conclusions

These preliminary results show that the current state-of-the-art for mesoporous and crystalline $TiO_2$ (250 $m^2/g$) can be reached using the self-synthesized PDMA-b-PS block copolymers. Nevertheless, much progress can still be made by varying the concentrations of polymers and Ti-precursor, adapting the temperature and moisture levels of the EISA-process and optimization of the thermal treatment. The nanocrystal route leaded to less satisfactory results, but only a few tests with unstable solutions were performed, where the block copolymer or the nanocrystals precipitated except for PDMA-$PS_{4k}$. Furthermore it will be investigated if a lower thermal treatment temperature (f.e. 375 °C) will lead to higher surface areas, as less of the mesoporous structure will collaps.

## *References*

1. Meynen V and Cool P, Microporous and Mesoporous Materials, 2009, **125**, 170.
2. Szeifert JM and Feckl JM, Journal of the American Chemical Society, 2010, **132**, 12605

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