Controlled Preparation of Inorganic-Organic Hybrid Polymers via the Atom Transfer Radical Polymerisation

G. Kickelbick, T. Gallauner, D. Holzinger, D. Rutzinger
Institut für Materialchemie, Technische Universität Wien, Getreidemarkt 9, A1060 Wien, Austria
E-mail: guido.kickelbick@tuwien.ac.at

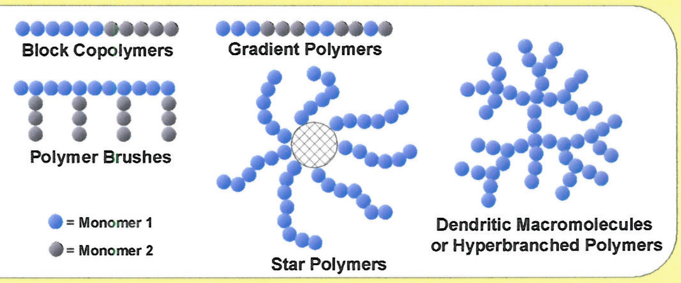
TU VIENNA — Technische Universität Wien — Vienna University of Technology

Introduction:
Inorganic-organic hybrid polymers are defined by the combination of the synergetic properties of their components, which often leads to dramatical changes in the mechanical, optical, or electronic properties of the final materials compared to the precursor compounds. Uncontrolled polymerisation methods, such as free radical polymerisation, were used for the majority of the materials until yet. Hence, there was limited possibility for an influence on the structure and composition of the polymer. Novel methods such as the transition metal catalysed atom transfer radical polymerisation (ATRP) open a novel field of research with respect to structural inorganic-organic hybrid materials.

Organic Component: Polymer
Preparation Method: Atom Transfer Radical Polymerization

Advantages of ATRP:
- Control of polymer morphologies
- Control of molecular weight
- Narrow molecular weight distribution
- Simple initiator molecules

Morphologies of the organic polymer that can be obtained:



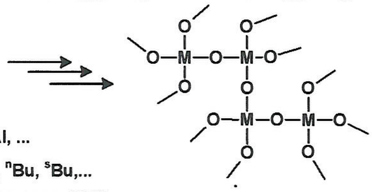
Inorganic Component: Metal Oxo Species
Preparation Method: Sol-Gel Process

Hydrolysis:

$$M(OR)_n \xrightarrow{H_2O} M(OR)_{n-m}(OH)_m + HOR$$

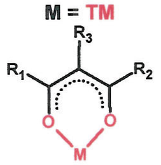
Condensation:

$$M(OR)_{n-m}(OH)_m \longrightarrow (RO)_{n-m}(HO)_mM{-}O{-}M(OR)_{n-m}(OH)_m$$



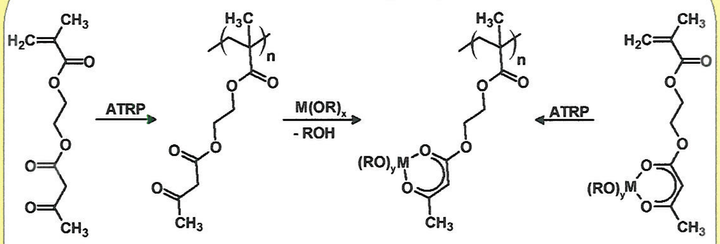
M = Si, Ti, Zr, Sn, Al, ...
R = Me, Et, ^{i}Pr, ^{n}Pr, ^{n}Bu, ^{s}Bu,...

Functional groups stable to hydrolysis
M = Si
R-H_2C-Si
M = TM



Mild process (RT)
Organic functionalisation of the inorganic moiety possible

Metal-Alkoxide Containing Polymers via ATRP

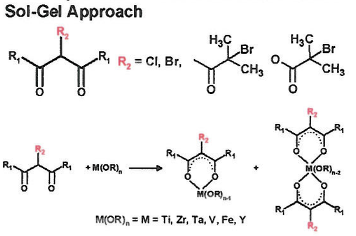


Preparation of homo-, random and diblock copolymers possible
Materials with very high mechanical strength
Reason: Crosslinking of polymer chains via ligand exchange reactions between the chains

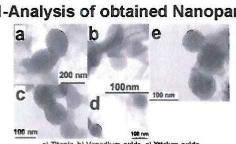
Inorganic Core Polymer Shell Nanoparticles

Amorphous Metal Oxide/Hydroxide Nanoparticles via a W/O-Microemulsions

Metal-Alkoxide Precursors for the Formation of Nanoparticles in a Microemulsion-Based Sol-Gel Approach

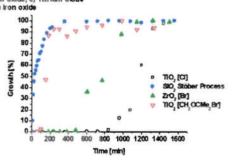


TEM-Analysis of obtained Nanoparticles



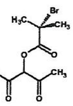
a) Titania, b) Vanadium oxide, c) Yttrium oxide d) Zirconium oxide, e) Iron oxide

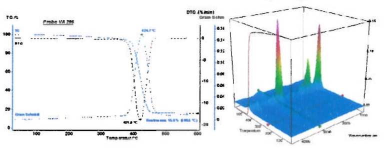
Particle growth measured by dynamic light scattering



Thermal Properties of Multifunctional Amorphous Particles Measured via TGA/FT-IR-Coupling

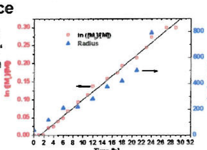
TiO_2 particles, Surface-Functionalized
Measured under an inert gas atmosphere

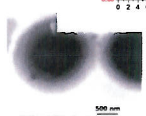




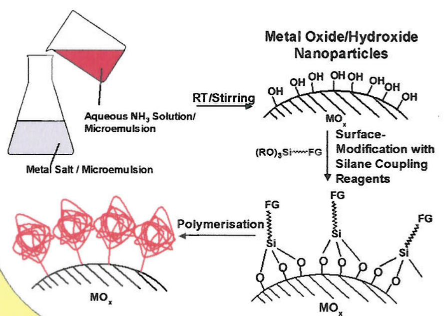
Grafting From Polymerization from Surface

Kinetics of the „grafting from" polymerisation

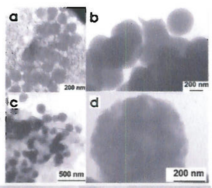




PMMA@TiO_2 Particles

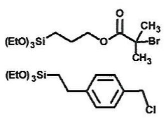


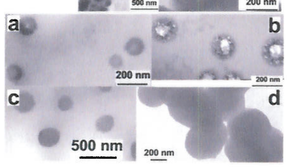
Metal salts: chlorides and nitrates
different rate of particle growth at similar reaction conditions



a) Iron Oxide, b) Titania
c) Zinc Oxide, d) Zirconium Oxide

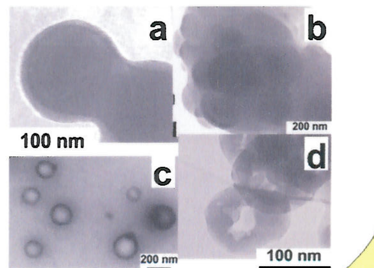
Surface-Modification





Coverage of the Particle Surface:
0,5 – 0,9 mmol/g

Metal Oxide/Polymer Shell Nanoparticles



Acknowledgement:
We thank the Fonds zur Förderung der wissenschaftlichen Forschung, Austria, for the financial support of this work and Dr. Ekkehard Füglein from Netzsch GmbH for the thermal analysis.