The ordering of dodecyl chains and their influence on the agglomeration of zirconia nanoparticles

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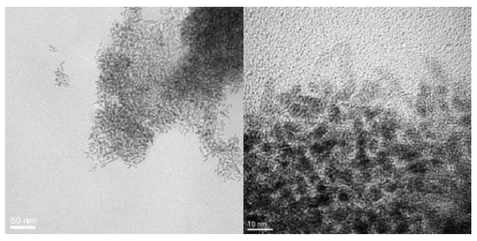
Introduction

The ordering of dodecyl chains has been investigated in mixed monolayers of phosphonic acid capping agents on the surface of hydrothermal prepared zirconia nanocrystals. As co-capping agent for the mixed monolayer formation, methyl-, phenyl-, pyryl- and *tert*-butyl phosphonic acid have been used to investigate series with different mixing ratios with dodecyl phosphonic acid. Here, the influence of the various molecules on the alkyl chain disordering is discussed. Small angle X-ray scattering (SAXS) studies show that with increasing amount of co-capping agent the agglomeration of the particles decreases. This behavior correlates with the ordering of the surface bond alkyl chains investigated by Fourier transform infrared spectroscopy (FTIR). This allows the conclusion that interparticle bilayers, formed via long alkyl chain packing, are responsible for the formation of dense particle agglomerates and can be controlled on a molecular level by co-adsorbing various molecules. [1]

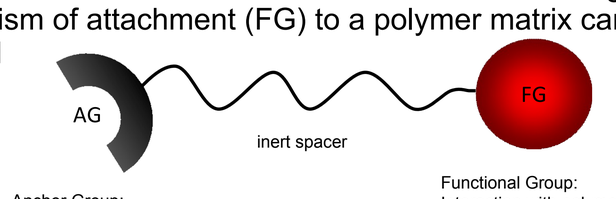
Material

ZrO_2 nanoparticles
- crystalline, monoclinic
- hydrothermally synthesized

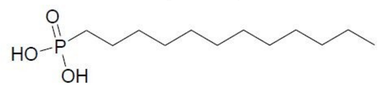


Capping agents:

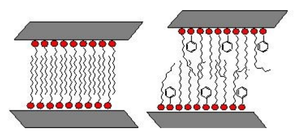
- Anchor group (AG) has to be tailored
- Spacer can be varied in its chemical behavior and length
- Mechanism of attachment (FG) to a polymer matrix can be controlled



Commonly used: Alkyl-Chain-moities



Problem:
Formation of self-assembled monolayers (SAM) using long alkyl chains
→ bilayer formation between two particles
→ creation of thermodynamic very stable agglomerates [2]



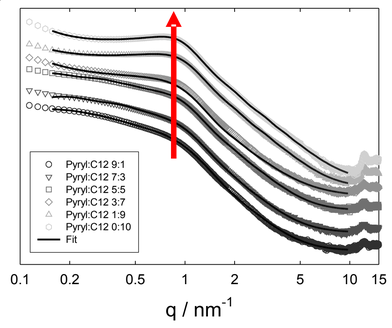
Solution: tuning of alkyl chain ordering via mixed monolayer formation

Small-angle X-ray scattering - Theory

Unified equation for the scattering Intensity by *Beaucage* [3] describing two functions – *Guinier's* law and a structurally limited power law

$$I(q) = \left(G \exp\left(\frac{-q^2 R_g^2}{3} \right) + B \left[\frac{(\mathrm{erf}(qR_g/\sqrt{6}))^3}{q} \right]^p \right) S(q)$$

G, B … numerical prefactors
p … *Porod* exponent
R_g … gyration radius



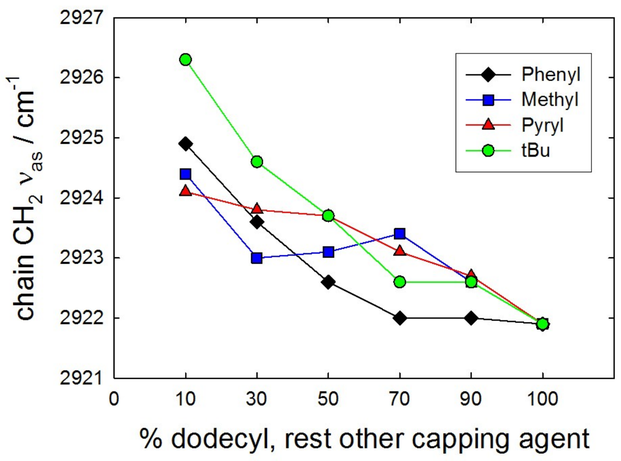
Structure factor *S(q)* to account for particle-particle interaction [4,5]

$$S(q) = \frac{1}{1 + 24\eta\, G(2qR_{HS})/(2qR_{HS})}$$

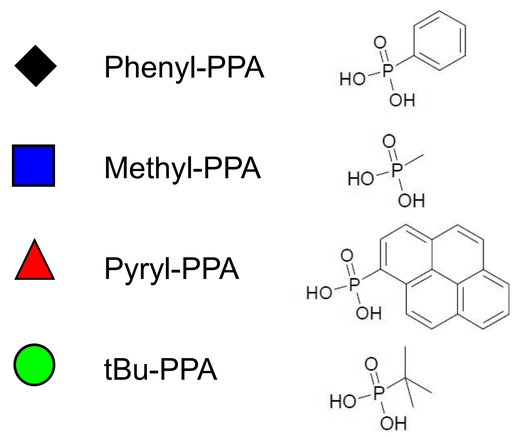
η... Hard-sphere volume fraction: Probability to find neighbouring particles
→ the higher η the higher the agglomeration of nanoparticles

RESULTS

FT-IR

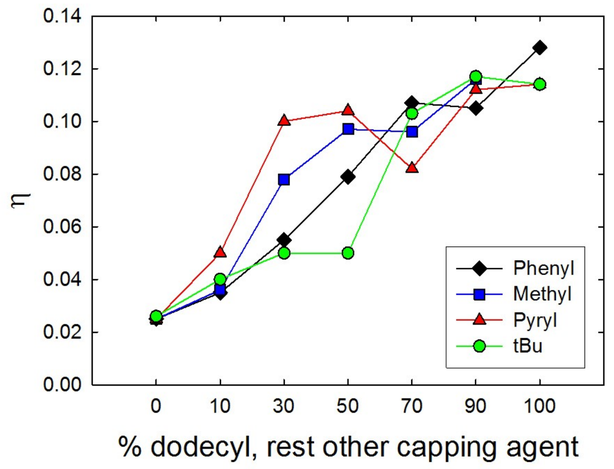


Ordering of alkyl chains disturbed by



Disorder of alkyl chains → observed by typical shift of the methylene C-H vibration of the C12 chain to higher wavenumbers

SAXS

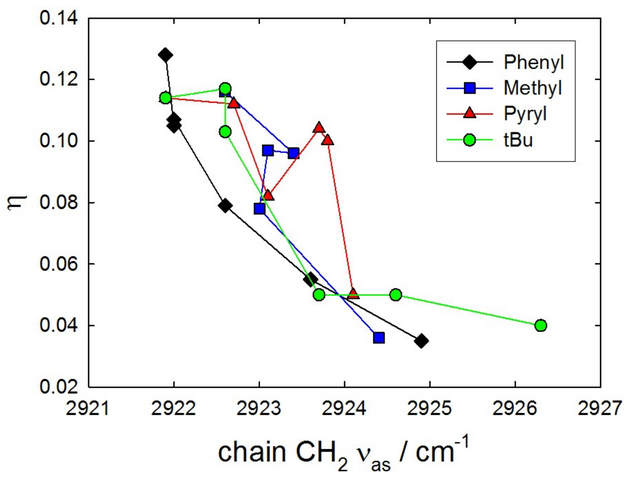


Disorder of alkyl chains → observed by decreasing agglomeration of nanoparticles

Disturbance of the so-called "zipper effect": bilayer structure between two neighbouring particles due to long alkyl chains

Dependence of alkyl chain disorder ability on co-capping molecule:

- Phenyl-PPA: almost linear trend of disordering with increasing amount
- Methyl-PPA: small molecule, no disorder at low amount
- Pyryl-PPA: bulky and planar, possible π–π interaction of extended aromatic system
- tBu-PPA: sterical demanding, most effective disordering



Correlation

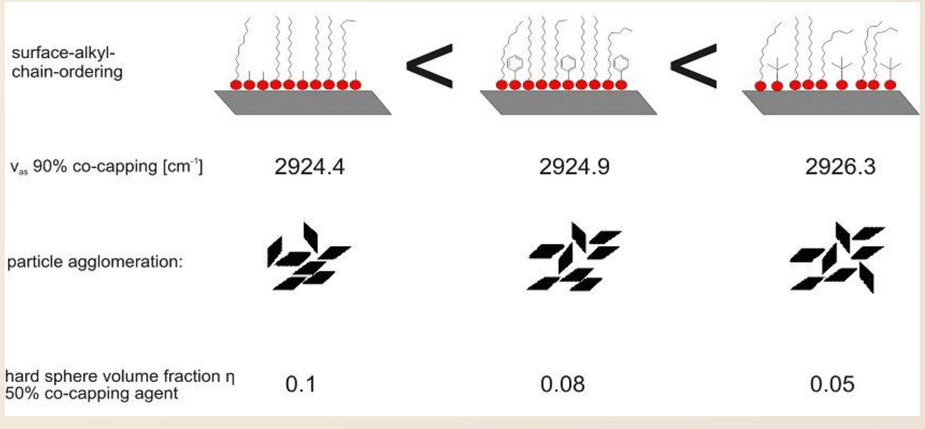
FT-IR studies:
disordering of dodecyl chains

SAXS studies:
agglomeration of nanoparticles

Summary

- Self-assembled monolayers (SAM) on nanoparticles with alkyl chains
- Controlled tuning of order/disorder
- Correlation of spectroscopical method (FT-IR) and structural method (SAXS):

→ Nanoparticles as probes for SAM-investigation with SAXS



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