Self-organized Nanostructures of Poly(4-vinylpyridine), Polyaniline and Polyamides due to Metal Complexation

*Sami Valkama[1], Juha Hartikainen[1], Mika Torkkeli[2], Ritva Serimaa[2], Janne Ruokolainen[1], Kari Rissanen[3], Gerrit ten Brinke[4], Olli Ikkala[1]**

1 Department of Engineering Physics and Mathematics, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Espoo, Finland
2 Department of Physics, University of Helsinki, P.O. Box 64, FIN-00014, Helsinki, Finland
3 Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40351, Jyväskylä, Finland
4 Department of Polymer Science and Materials Science Center, Dutch Polymer Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Summary: Comb-shaped supramolecules are constructed using flexible polymers and semi-rigid conjugated undoped or doped conjugated polymers upon complexing Zinc dodecyl benzene sulphonate, $Zn(DBS)_2$. Self-organized nanostructures are formed in the bulk due to competing attractive interactions (coordination or water mediated hydrogen bonding) and repulsive polar/nonpolar interactions, showing characteristic long periods of ca. 30 Å.

Introduction

Supramolecules are molecular level entities, which form due to specific physical interactions (recognition).[1,2] *Homopolymer-like supramolecules* can be constructed by connecting repeat units eg. by coordination[3] or combinations of hydrogen bonds[4]. *Block copolymer-like supramolecules* can be obtained particularly straightforwardly using eg. the comb-shaped architecture[5-7] as it allows a means to efficiently control the processibility of even rigid polymers[8] and to obtain self-organized nanostructures in bulk. In general, synthesis of supramolecules can be challenging due to the need of molecularly matching interactions. By contrast, we discuss in this report facile and economic concepts, which may not necessarily be optimal in their geometry, but which are sufficient to provide supramolecules and nanoscale order and therefore tailored

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properties. Zinc dodecyl benzene sulphonate, i.e. $Zn(DBS)_2$, is a useful model compound due to the coordination capability of Zn^{2+} in the combination of nitrogen containing polymers poly(4-vinyl pyridine) (P4VP)[9], polyaniline (PANI)[10,11] and polyamide 6 (PA6).

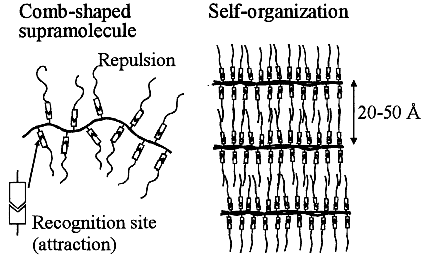

Figure 1. The concept to form comb-shaped supramolecules and their self-organized *block-copolymer-like* nanostructures.

Poly(4-vinylpyridine)

The oligomeric pyridine groups are known to coordinate with several transition metals.[12] Also Zn^{2+} forms coordination with oligomeric vinylpyridine to allow eg. tetrahedral geometry with $ZnCl_2$.[12] In the polymeric case, the four-coordinated P4VP-complexes with Cu^{2+} in aqueous solutions lead to crosslinking.[13] The steric hindrance may, however, limit the allowed geometries in the polymeric case, as was discussed in the context of $ZnCl_2$ complexation with P4VP.[12] By complexing $Zn(DBS)_2$ with P4VP, we obtain characteristic[14,15] FTIR changes in the pyridine ring stretching that can be assigned to coordination, see Figure 2. Note that the Zinc sulphonate moieties are very hygroscopic and water molecules may easily be additionally bonded. Small Angle X-ray Scattering (SAXS) shows scattering peak at the magnitude of scattering vector $q \approx 0.22$ $Å^{-1}$. No higher order peaks were resolved. Note, that the corresponding hydrogen bonded complexes with alkylphenols also showed only a relatively weak second order peak, even if the lamellar structure was revealed by TEM.[6] We suggest that the structure is lamellar with a relatively poor order in the present case.[9]

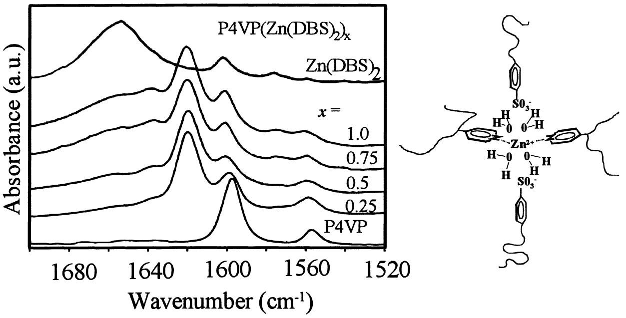

Figure 2. FTIR of P4VP(Zn(DBS)$_2$)$_x$, showing that the typical pyridine ring absorption at 1597cm^{-1} is suppressed upon complexation and instead a band at 1617cm^{-1} is observed.[9] Also, a potential scheme for bonding is shown, illustrating coordination which may connect two P4VP chains. In addition absorbed water molecules are expected.

Unprotonated polyaniline

Polyaniline is one of the most important conjugated polymers due to its stability and economics. In the undoped form, i.e. emeraldine base, it consists of alternating quinone diimine and benzene diamine moieties. Upon complexation, small FTIR shifts are observed in the bands corresponding to the imine groups, also showing concurrent changes in the UV/Vis spectra, indicating coordination to the iminic nitrogens.[10] The bonding geometry is not yet known. Zn^{2+} may form bridging between two PANI chains, as has been discussed previously for PANI/Ru-complexes.[16] Self-organized lamellar structures are observed based on SAXS, see Fig. 3

Sulfonic acid protonated polyaniline

Conceptually different situation is observed if the iminic nitrogens of PANI are first protonated using dodecyl benzene sulphonic acid (DBSA) to form nominally PANI(DBSA)$_{0.5}$. Astonishingly, even in that case, SAXS suggests self-organized lamellar phases.[11] However, FTIR did not unambiguously reveal the complexation sites. Model studies with

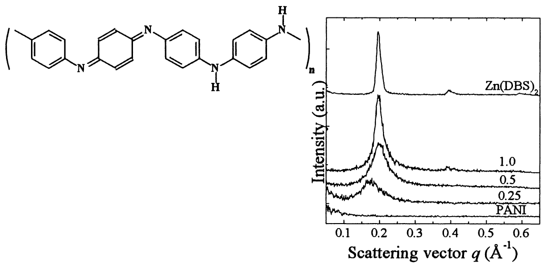

Figure 3. Emeraldine base form of PANI and the SAXS patterns of its complexes with $Zn(DBS)_2$.[10] The magnitude of the scattering vector is given by $q=(4\pi/\lambda)\sin\theta$ where 2θ is the scattering angle and $\lambda=1.542$ Å.

related oligomeric compounds (see Figure 4) allowed to grow single crystals to assign the structures in detail and showed that Zinc sulphonates can be bonded to the sulphonates of the protonating sulphonic acids by water mediated hydrogen bonding.[11] Figure 4 shows the suggested bonding in the case of $PANI(DBSA)_{0.5}$ complexed with $Zn(DBS)_2$.

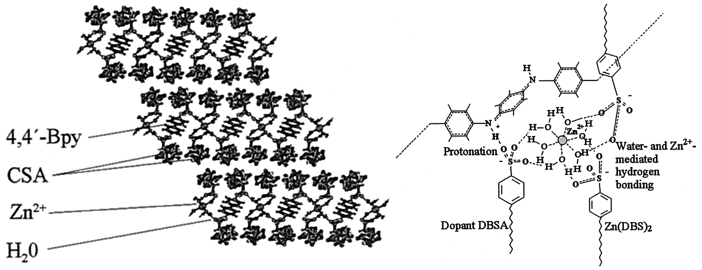

Figure 4. The resolved crystalline structure for a complex consisting of 4,4′-bipyridine where both pyridine rings have been protonated by camphor sulphonic acid (CSA) and where two zinc camphor sulphonate molecules have been complexed by water mediated hydrogen bonding.[11] So far tentatively, such bonding is also suggested between $PANI(DBSA)_{0.5}$ and $Zn(DBS)_2$.[11]

Polyamide 6

Coordination complexation of $Zn(DBS)_2$ takes place also with amide-containing polymers, e.g. polyamides. However, the coordination mechanisms is different than in the

P4VP case. Now the coordination bond is formed between Zn^{2+} and the oxygen atom of the amide carbonyl. FTIR-spectrum of $PA6[Zn(DBS)_2]_{1.00}$ in Figure 5 illustrates the formation of coordination bond as a shift of the characteristic amide I vibration (C=O stretching vibrations) to lower wavenumbers (from 1640 cm^{-1} to 1617 cm^{-1}). For neat $Zn(DBS)_2$, a self-organized layered structure with long period of ca. 33 Å is observed. The $PA6[Zn(DBS)_2]_{1.00}$ shows a distinct intensity maximum at the q-value of ca. 0.20 $Å^{-1}$ and a second very flat intensity maximum at q = 0.40-0.42 $Å^{-1}$ suggesting that lamellar structures are formed. Note that, it turned out that the complexes were metastable and macrophase separation was observed during several months. This problem may be avoided by using different metal cations in the amphiphilic molecules or using $Zn(DBS)_2$ with more branched alkyl chains, which suppresses its tendency of phase separation due crystallization.

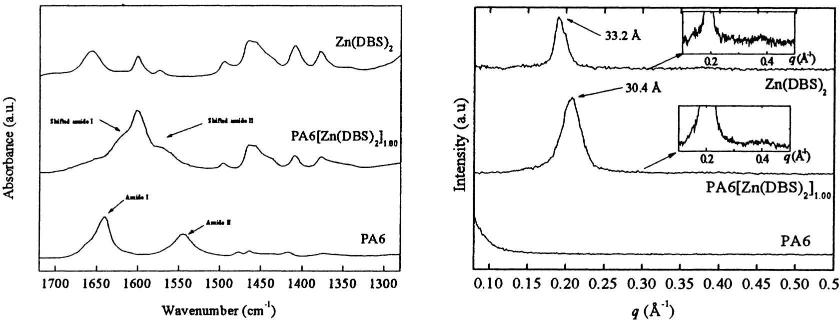

Figure 5. FTIR-spectra of $PA6[Zn(DBS)_2]_{1.00}$, $Zn(DBS)_2$ and PA6 in the 1700-1300 cm^{-1} region. Also the SAXS intensity patterns of $PA6[Zn(DBS)_2]_{1.00}$, $Zn(DBS)_2$ and PA6 are shown The magnitude of the scattering vector is given by $q=(4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ=1.542 Å. The scattering intensity is in a linear scale.

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