Comb-Shaped Supramolecules of Emeraldine Base Form of Polyaniline Due to Coordination with Zinc Dodecyl Benzenesulfonate and Their Plasticized Self-Organized Structures

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ABSTRACT: We show that the emeraldine base form of polyaniline (PANI) forms self-organized (mesomorphic) structures upon mixing with an amphiphilic oligomer zinc dodecyl benzenesulfonate, Zn(DBS)$_2$. The number of Zn(DBS)$_2$ molecules vs the number of PhN repeat units of PANI was selected to be $x = 0$, 0.125, 0.25, 0.5, and 1.0, and the mixtures were denoted as PANI[Zn(DBS)$_2$]$_x$ according to their nominal compositions. PANI consists of alternating quinone diimine and benzene diamine groups. FT-IR and UV−vis spectroscopies reveal changes in the quinone diimine moieties upon adding Zn(DBS)$_2$, thus suggesting coordination to the iminic nitrogens to form comb-shaped supramolecules PANI[Zn(DBS)$_2$]$_{0.5}$. Their structure formation was studied using small-angle X-ray scattering and electron microscopy. The competition between the attraction (coordination) and repulsion (dodecyl tails) leads to a self-organized lamellar phase with a long period of ca. 31 Å. Further increase of Zn(DBS)$_2$ did not reveal clear changes in FT-IR and UV−vis but results in plasticization to render viscous fluid upon heating for $x = 1.0$, in contrast to the uncomplexed PANI which is infusible.

Introduction

Block copolymers form self-organized nanoscale structures due to repulsion between the covalently connected blocks.[1,2] The blocks can also consist of rigid and conjugated polymers or oligomers[3,4] or contain side chain liquid crystalline moieties.[5] In the comb-shaped architecture,[6] the self-organization takes place essentially similarly. A special case consists of so-called hairy rods where there are flexible side chains covalently bonded to rigid backbones.[7,8] There the comb-shaped architecture is of special importance as it also induces fusibility and solubility in a straightforward way to the otherwise intractable backbone. In comb-shaped polymers, the attractive covalent, i.e., permanent, interaction between the backbone and the repulsive side chains can be replaced by weaker carefully matched physical interactions (recognition) to form supramolecules (for supramolecular chemistry, see refs 9 and 10) which may analogically lead to self-organized (mesomorphic) structures, as demonstrated using flexible[11−16] and more rigid[17−20] backbones.

Metal coordination is a versatile interaction: For relatively low molecular weight compounds, the coordination geometries and the molecular structures have been carefully matched to allow complicated well-defined supramolecules based on metal coordination.[9,10,21] Such assemblies typically segregate as single crystals from solutions. In high molecular weight polymers, such well-defined bonding geometries and single crystals may be less expected, and metal complexes have in this case usually been discussed in a slightly different context; e.g., in general to modify polymer and blend properties,[22,23] due to their biological functions,[24] and more specifically the transition metal coordination in poly(vinylpyridine)s has been studied to modify polymer properties[25,26] and to achieve self-organized structures.[27] In the last case, supramolecules based on poly(4-vinylpyridine) are formed by coordinating zinc dodecyl benzenesulfonate, Zn(DBS)$_2$, and the supramolecules undergo self-organization. The metal cation coordinates to the nitrogen lone electron pair with an empty orbital, and the two nonpolar dodecyl tails provide a repulsion from the polar polymer backbone.

In this paper we extend the concept to prepare supramolecules based on conjugated nitrogen-containing polymer, i.e., polyaniline (PANI) emeraldine base,[28] due to coordination with Zn(DBS)$_2$. The supramolecule formation is in this case nontrivial due to the quite rigid nature of PANI. Such polymers are typically infusible and poorly soluble in common solvents, i.e., “intractable”, and macroscopic phase separation in mixtures easily takes place, unless the attraction proves to be particularly strong.

The nonconducting emeraldine base nominally consists of alternating benzene diamine and quinone diimine units, as shown in Scheme 1. In the conventional acid doping, the iminic nitrogens of PANI are protonated, and an acid−base complex is formed, i.e., an emeraldine salt, which is electrically conductive.[29,30] In particular, when the iminic nitrogens are protonated by an amphiphilic acid dodecyl benzenesulfonic acid (DBSA), an infusible conducting crystalline (orthorhombic) salt PANI(DBSA)$_{0.5}$ is formed,[31] but when additionally the aminic nitrogens are hydrogen bonded with DBSA, a self-organized lamellar (noncrystalline) material is

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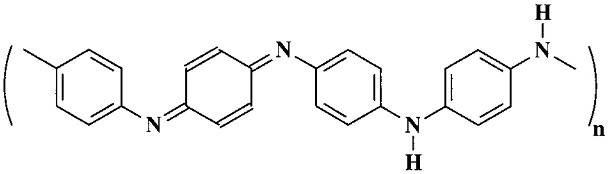
formed.[19] Self-organization requires that the protonic acid has a long alkyl chain to allow sufficient repulsion.



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In addition to protonic acids, also organic electron acceptors and Lewis acids can be used to dope EB.[32−34] Also in this case such as using zinc chloride the complexation occurs at the iminic nitrogen sites of PANI due to their higher reactivity and may induce an effect somewhat similar to protonic acid doping. The doping in these cases is, however, less effective than that based on protonic acids. The preference of the iminic sites has also been reported when LiCl is added to PANI.[35] In the present study, we use coordination of emeraldine base form of PANI with Zn^{2+} cation not to achieve conductivity but to demonstrate comb-shaped supramolecules where the repulsive combs cause plasticization and self-organization.

Experimental Section

Materials. Emeraldine base (subsequently denoted as PANI) was synthesized by PANIPOL Ltd. (Finland). The molecular weight was $M_w = 52\,000$ g/mol and polydispersity 3.1, as measured with GPC using normal procedures.[36] PANI was dried for 24 h in a vacuum (level 10^{-2} mbar) at 25 °C. DBSA was of laboratory purity and was obtained from Tokyo Kasei. NMR studies reveal that it contains branched alkyl chains, and the structure is actually $(C_mH_{2m+1})(C_nH_{2n+1})CH-C_6H_4-SO_3H$ where $m + n + 1 = 10-14$, dominantly 12. ZnO was supplied by J.T. Baker B.V. The solvents were of analysis grade and dried using 3 Å molecular sieves. All reagents were used as received.

$Zn(DBS)_2$ was prepared from DBSA and ZnO in anhydrous ethanol according to the procedure described previously[27] and dried for 24 h in a vacuum (level 10^{-2} mbar) at 60 °C and for 24 h in 80 °C. In this work, the material was additionally purified by recrystallizing three times in acetone by adding distilled water dropwise and finally dried for 24 h at 80 °C in a vacuum.

The complexes were prepared by dissolving PANI in *N*-methylpyrrolidone (NMP) to 1.0 wt % solution. $Zn(DBS)_2$ was also dissolved in NMP. The solutions were mixed and stirred for 24 h at room temperature in closed vessels. During mixing the solutions were clear. The solvent was evaporated from Petri dishes on a hot plate at 60 °C, and the products were dried for 24 h in a vacuum (level $<10^{-2}$ mbar) at 60 °C and 24 h at 80 °C. The nominal degree of complexation x in PANI[$Zn(DBS)_2$]$_x$ (mol of $Zn(DBS)_2$ vs mol of repeat units of PANI) was selected to be 0.125, 0.25, 0.5, and 1.0. Also, reference samples of PANI and $Zn(DBS)_2$ were prepared from NMP according to the same procedure.

FT-IR. The transmission FT-IR spectra were recorded with a Nicolet Magna IR 750 FT-IR spectrometer equipped with a DTGS detector. Samples were prepared from NMP solution on potassium bromide crystals.

UV/Vis. Spectra were measured using Hitachi D-2000 spectrophotometer. Samples were solvent cast from NMP solution on quartz substrates.

Optical Microscopy. The optical observations were carried out using a Nikon Optishot 66 microscope in transmission mode with a Linkam TMS 91 hot stage. The samples were prepared as thin films between two glass plates.

SAXS. Small-angle X-ray scattering was performed at room temperature as described previously.[37]

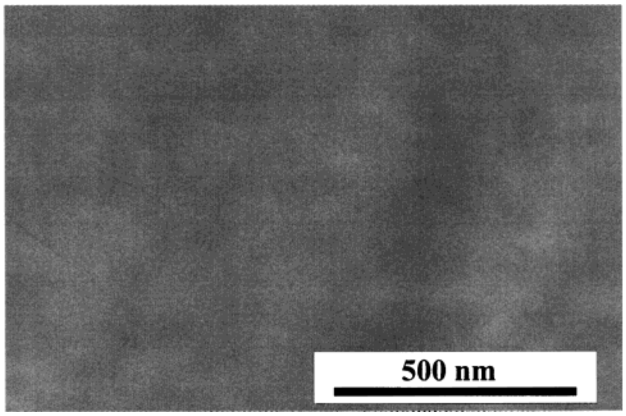

Figure 1. SEM micrograph of PANI[$Zn(DBS)_2$]$_{0.5}$.

TEM. Ultrathin sections were cut from the epoxy embedded bulk specimen using a Leica Ultracut UCT ultramicrotome and a diamond knife at −50 °C. Transmission electron microscopy was performed as described before[38] with the exception that the samples did not require staining.

SEM. Field emission scanning electron microscope Hitachi S-4300 operated at acceleration voltage of 2.0 kV was used.

Elementary Analysis. The degree of complexation was studied using elementary analysis by measuring the sulfur/nitrogen weight ratio (S/N). Nitrogen contents was analyzed using LECO CHN analyzer and sulfur content using Ströhlein analyzer. In this study the composition of PANI[$Zn(DBS)_2$]$_x$ was selected to $x = 0.5$. The calculated S/N ratio for this composition is 2.28, and the observed ratio was S/N = 2.0, which corresponds to the degree of complexation $x = 0.44$. Unfortunately, the NMP solvent also contains nitrogen, and due to the high boiling point, it is relatively difficult to remove completely. Only 3 wt % trace of NMP is sufficient to change the S/N ratio to 2.0 for $x = 0.5$.

Results and Discussion

We first study whether there is evidence on attractive interaction between PANI and $Zn(DBS)_2$ in their mixtures which would suppress the tendency for macroscopic phase separation. Pure emeraldine base does not melt and cross-links easily upon heating due to reactivity of the iminic sites. The composition with PANI[$Zn(DBS)_2$]$_{0.25}$ is hard and does not soften upon heating. However, an increase of $Zn(DBS)_2$ renders progressively softened material, and for example PANI[$Zn(DBS)_2$]$_{1.0}$ can be a “melt” near 200 °C to become a viscous fluid on a hot plate between two microscope glass plates and allows a homogeneous film without clear particles at the resolution of an optical microscope. To illustrate the homogeneity of the mixtures in more detail, Figure 1 depicts a SEM micrograph for PANI[$Zn(DBS)_2$]$_{0.5}$ which shows a uniform structure without resolvable dispersed particles at the submicron length scale. Such observations support the hypothesis that PANI dissolves in $Zn(DBS)_2$ at these high concentrations which indicates their attraction. That the mixtures can be heated to render viscous homogeneous fluid indirectly also suggests that the cross-linking tendency of pure PANI at the iminic sites is suppressed which would indicate complexation with $Zn(DBS)_2$. Analogical behavior is well-known for acid protonated PANI where the protonation at the iminic sites causes increased thermal stability against cross-linking.[39]

Direct spectroscopic evidence for the complex formation is obtained based on FT-IR and UV/Vis. Figure 2 depicts the FTIR absorption at the 1400−1700 cm^{-1} bands. For pure emeraldine base ($x = 0$), the band

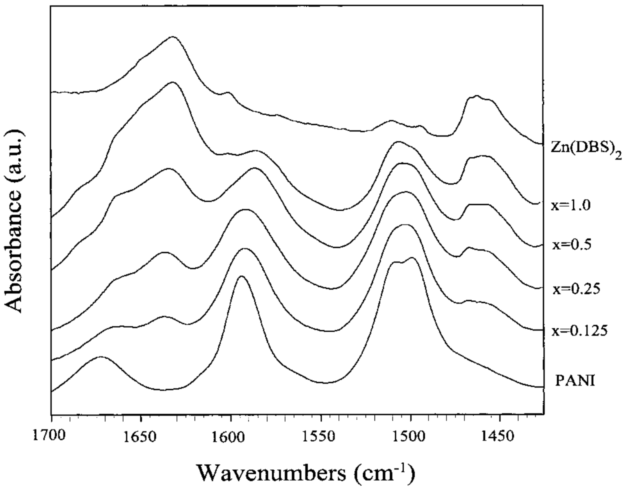

Figure 2. FT-IR spectra of PANI[Zn(DBS)$_2$]$_x$ for $x = 0.125$, 0.25, 0.5, and 1.0, as well as for PANI emeraldine base and Zn(DBS)$_2$.

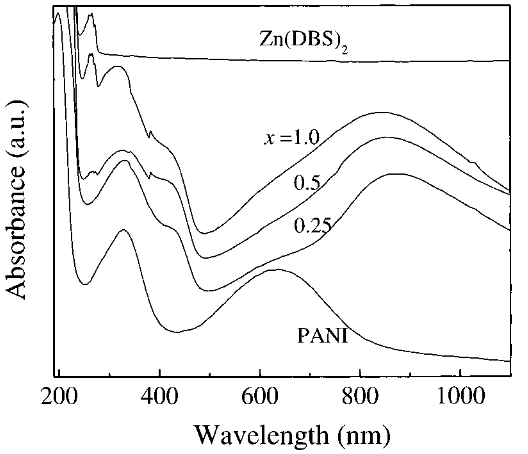

Figure 3. UV–vis -spectra of PANI[Zn(DBS)$_2$]$_x$ for $x = 0.25$, 0.5, and 1.0, as well as for PANI emeraldine base and Zn(DBS)$_2$.

corresponding to the quinoid ring stretching is located at 1593 cm^{-1} and the benzenoic ring stretching near 1500 cm^{-1}.[40–44] Upon adding Zn(DBS)$_2$, the latter peaks do not undergo clear shifts whereas the quinoid peak shifts to lower wavenumbers: $x = 0$, 1593 cm^{-1}; $x = 0.125$, 1591 cm^{-1}; $x = 0.25$, 1590 cm^{-1}; $x = 0.5$, 1586 cm^{-1}; $x = 1.0$, 1585 cm^{-1}. Therefore, a small but clear stepwise change of ca. 4 cm^{-1} takes place upon increase from $x = 0.25$ to 0.5. We regard this observation as an evidence to support complexation to the imines. Note that in protonation the shift is similar but much larger, and in this case also the benzenoic ring stretching undergoes a shift.[40,44]

Further evidence is obtained from UV–vis spectroscopy. The uncomplexed PANI (see Figure 3) shows absorption at 327 nm (a π–π* transition) and at 631 nm (excitation band of the quinoid ring).[45] For PANI[Zn(DBS)$_2$]$_x$ with $x = 0.25$, 0.5, and 1.0 the absorption spectra are totally different, as characteristic of doped polyaniline: the quinoid band is not observed whereas localized polaron bands at 430 and ca. 860 nm are observed.[45,46] Such spectra are typical for poorly conducting doped PANI with localized charge carriers.

The nature of the complexation of Zn(DBS)$_2$ to the iminic sites deserves further comments. Zn^{2+} is known to coordinate with nitrogen-containing groups.[21] For example, in pyridine-containing oligomers, tetrahedral arrangement is typically observed with four ligands for each Zn^{2+}.[47,48] Therefore, coordination is suggested also in the present case: As the sulfonate group occupies one coordination site, each Zn^{2+} would ideally coordinate to two dodecyl benzenesulfonates of the same Zn(DBS)$_2$ molecules, as well as to two iminic nitrogens of PANI chains. This stoichiometry could suggest coordinative cross-linking due to bridging between two PANI chains, as discussed in the context of ZnCl$_2$ complexed poly(vinylpyridine).[48] However, in polymeric materials the steric hindrances due to the polymer chains may distort the achievable structures.[23,47] In the present case of Zn(DBS)$_2$ complexation with PANI, as well as with P4VP,[27] the coordinative cross-linking is not probable, as the materials become viscous fluids upon heating. Furthermore, the additional steric hindrance due to the dodecyl tails may further suppress the tendency for Zn^{2+} to form bridges between two chains. Thus, there may exist steric difficulties for a Zn(DBS)$_2$ molecule complexed to an imine of one PANI chain to fill the fourth coordination site using an imine group of another polymer chain. Therefore, the fourth site might be susceptible to bond potential solvent residuals or water due to the hygroscopic nature of the materials, as discussed also for poly(vinylpyridine) coordinated with ZnCl$_2$.[48]

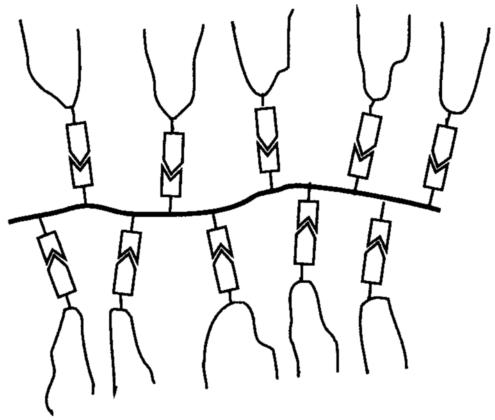

Figure 4. Schematics of the supramolecule formation between PANI and Zn(DBS)$_2$ molecules. Recognition due to coordination is indicated as well as the two repulsive dodecyl tails of Zn(DBS)$_2$.

In conclusion, the above considerations suggest coordination to the iminic nitrogens to allow supramolecules PANI[Zn(DBS)$_2$]$_{0.5}$. Because of the dodecyl tails, such supramolecules are comb-shaped, schematically shown in Figure 4. As the “combs” are repulsive to the backbone, it can be questioned whether the supramolecules self-organize. SAXS does not show any scattering peaks of PANI (see Figure 5), whereas for $x = 0.25$ a very shallow and broad peak is observed at $k = 0.171$ Å^{-1}. For $x = 0.5$ a more pronounced scattering peak is obtained at $k = 0.197$ Å^{-1}, suggesting self-organization. But as it is still relatively broad and no higher order peaks are resolved, the structure cannot be inferred solely on the basis of SAXS. However, combination with TEM (see Figure 6) allows to suggest a lamellar self-organized local structure with a long period of 32 Å with a relatively poor overall order. Note that the poor overall order is in contrast to the previously reported TEM results concerning another polymer–amphiphile complex, i.e., poly(4-vinylpyridine) hydrogen bonded with nonadecylphenol,[38] which shows highly ordered lamellae. In the present case, the less developed order may

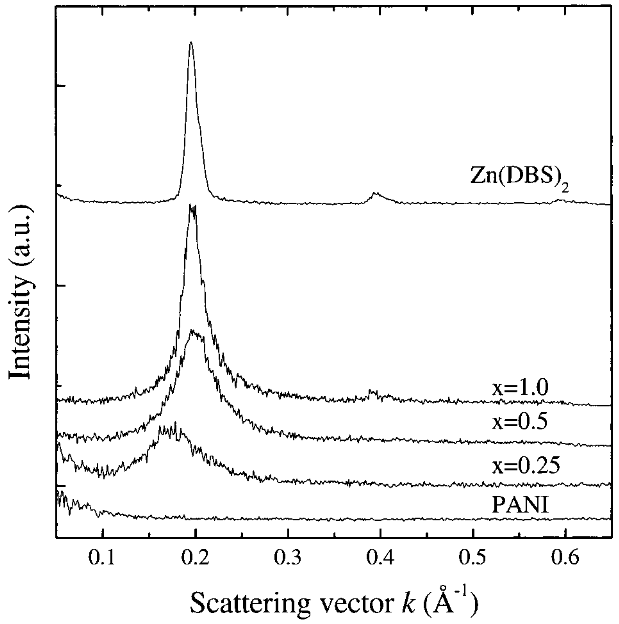

Figure 5. SAXS intensity patterns of PANI[Zn(DBS)$_2$]$_x$, x = 0.25, 0.5, 1.0, and PANI, and Zn(DBS)$_2$. The magnitude of the scattering vector is given by $k = (4\pi/\lambda)\sin\theta$ where 2θ is the scattering angle and $\lambda = 1.542$ Å.

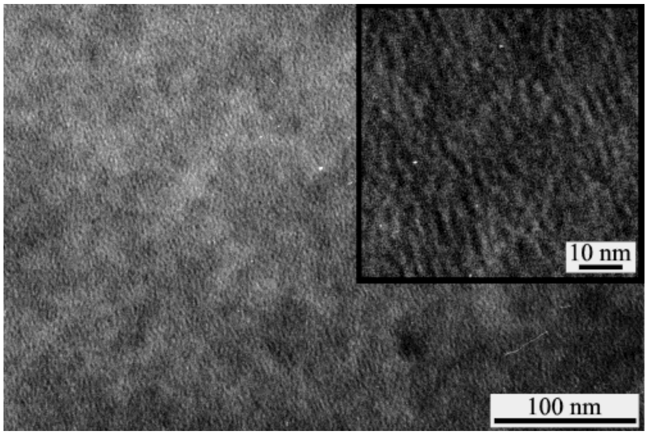

Figure 6. TEM micrograph of PANI[Zn(DBS)$_2$]$_{0.5}$.

be due to the more rigid polymer and poorer plasticization. Another aspect in relation to Figure 6 is that no evidence on uncomplexed dispersed particles were observed even at this high resolution.

We will next consider the composition with nominally one Zn(DBS)$_2$ vs each aromatic repeat unit of PANI, i.e., $x = 1.0$. As was pointed out before, increased amount of Zn(DBS)$_2$ causes plasticization. The question remains whether the additional Zn(DBS)$_2$ is bonded to PANI[Zn(DBS)$_2$]$_{0.5}$ and, in particular, what would be the nature of such potential interaction. FT-IR and UV–vis did not provide answers in this direction (Figures 2 and 3). SAXS shows that increasing the amount of Zn(DBS)$_2$ renders only more "Zn(DBS)$_2$-type" scattering peaks (see Figure 5). Therefore, at present the potential bonding of additional Zn(DBS)$_2$ to PANI[Zn(DBS)$_2$]$_{0.5}$ remains open. The problem may be complicated, and the hygroscopic nature of the materials could play a role. Note that usually the crystalline zinc sulfonates contain crystalline water. Even the ordering of Zn(DBS)$_2$ depends on the amount of absorbed water: Carefully dried Zn(DBS)$_2$ is smectic mesomorphic whereas water absorption renders a crystalline material.[49] In the present work, even when the materials have been dried and they are stored under anhydrous conditions, one cannot exclude the possibility that there would be slight amounts of water absorbed during the characterization stages. Absorbed water might play a role in the possible interaction between the additional Zn(DBS)$_2$ and PANI[Zn(DBS)$_2$]$_{0.5}$.

Concluding Remarks

Mixtures of PANI and Zn(DBS)$_2$ were prepared and investigated using FT-IR, SAXS, optical microscopy, TEM, and SEM. A composition with 0.5 mol of Zn(DBS)$_2$ vs 1 mol of PANI PhN repeat units leads to supramolecules due to complexation, and the resulting PANI[Zn(DBS)$_2$]$_{0.5}$ exhibits essentially nonconducting self-organized lamellar structure with a long period of 31 Å. The iminic nitrogens in PANI form coordination bonds with the zinc cations. Further addition of Zn(DBS)$_2$ plasticize the material to allow "melting". The complexation of nonprotonated PANI with amphiphiles opens new possibilities to process PANI from the melt and solutions, as the surfactant alkyl chain can be tailored to increase sufficient solubility in some solvents in analogy with the hairy rods. In addition, the amphiphiles are soluble in common solvents and can therefore be easily removed after processing, if necessary.

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