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Nanoscale Conducting Cylinders Based on Self-Organization of Hydrogen-Bonded Polyaniline Supramolecules

Harri Kosonen,[†] Janne Ruokolainen,[†] Matti Knaapila,[†] Mika Torkkeli,[‡] Kaija Jokela,[‡] Ritva Serimaa,[‡] Gerrit ten Brinke,[†,#] Wim Bras,[§] Andrew P. Monkman,[*,⊥] and Olli Ikkala[*,†]

Department of Engineering Physics and Mathematics, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Espoo, Finland; Department of Physics, University of Helsinki, P.O. Box 9, FIN-00014 Helsinki, Finland; Netherlands Organization for Scientific Research (NWO) DUBBLE CRG/ESRF, c/o BP 220, Grenoble F38043, France; Department of Physics, University of Durham, Durham DH1 3LE, UK; and Department of Polymer Science and Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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ABSTRACT: Comb-shaped or hairy rodlike supramolecules can be obtained by hydrogen bonding rigid rod polymers and amphiphilic oligomers. Here we introduce a concept to achieve electrically conducting acid doped PANI to allow cylindrical self-organization. PANI is doped with camphorsulfonic acid (CSA) where 4-hexylresorcinol (Hres) is hydrogen bonded to form supramolecules, which further undergo self-organization. The structure formation of PANI(CSA)$_{0.5}$(Hres)$_y$ complexes is discussed on the basis of small- and wide-angle X-ray scattering and electrical conductivity. Highly ordered hexagonal cylindrical structures were observed with a distance between the cylinders around 35 Å. Electrical conductivity increases 2 orders of magnitude upon formation of cylindrical structures, potentially due to confinement of PANI chains within the cylinders. The method would then allow an easy preparation of nanoscale organic conducting wires, just by mixing the components together.

Introduction

Competing interactions can be used in molecular engineering of synthetic polymers to render nanoscale structuring by self-organization.[1] Such concepts give rise to functional or controllable materials,[2,3] in analogy with many biological systems. Among the simplest materials to do this are block copolymers of flexible polymers, which form self-organized spherical, cylindrical, gyroid, and lamellar structures.[4] Also, rigid blocks can be incorporated which offers possibilities to combine liquid crystallinity and self-organization,[5,6] as well as to allow other structures.[7,8] Another example consists of so-called hairy rod polymers, which are rigid polymers having a dense set of flexible side chains (such as alkyl tails) covalently bonded to the backbone.[9] Therefore, they constitute a special case of comb copolymers, and the repulsion between the alkyl tails and the rigid backbone controls self-organized structures. In the case of undoped conjugated polymers,[10] the structure formation in poly(alkylthiophene)s,[11] poly(alkylphenylene)s,[12] poly(alkoxyphenylene)s,[13] and poly(phenylene)s with oligomeric ethylene oxide side chains[14] has been described. Typically, a lamellar structure with a periodicity of 20−30 Å is obtained. However, in some cases, such as butoxy-modified polyphenylene,[13] a cylindrical self-organization is obtained. However, doping disturbs the structure formation.[15]

In the comb copolymers the covalent bonds between the side chains and the backbone can be replaced by weaker physical bonds, such as ionic interaction,[16,17] coordination,[18] and hydrogen bond.[19,20] In such cases the self-organizing units are not chemically bonded comb-shaped molecules but can be classified as physically bonded polymer−surfactant or polymer−amphiphile supramolecules. (For an overview of supramolecular chemistry, see refs 21 and 22.) In the conjugated polymers, lamellar self-organization in polypyrrole−alkyl sulfates[23] and polyaniline−dodecylbenzenesulfonates[24] have been observed. For polyaniline, protonation by strong acids,[25,26] such as sulfonic acids, is known to simultaneously render conducting polymeric salts.

In this work we pose the following question. In carbon nanotubes[27] and columnar self-organized other carbon nanostructures,[28] interesting one-dimensional transport properties have been obtained. Our aim is to identify concepts to form supramolecules consisting of conducting PANI salts and amphiphiles with matching physical bonds to allow cylindrical self-organization. Two options are at hand: either (I) to modify the dopant, i.e., the strongly acidic molecule, to incorporate a suitable end group or (II) to perform the doping (protonation) and the structure formation using different bonded molecules. The latter concept seemed more appealing as it is a more flexible concept to allow molecular engineering. However, it turned out to be surprisingly difficult to realize, and so far, we have identified only one concept: the iminic nitrogens of polyaniline (PANI) are nominally fully doped using camphorsulfonic acid (CSA)[29] to yield PANI(CSA)$_{0.5}$ and where 4-hexylresorcinol (Hres) is further hydrogen bonded. Both of the two hydroxyl groups of Hres are needed to prevent macrophase separation. This is in agreement with our previous observations in poly(p-pyridine)s where more than one hydrogen bond is needed to prevent macroscopic phase separation to achieve self-organized structures.[30] In the present work we investigate the structure forma-

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[†] Helsinki University of Technology.
[‡] Helsinki University.
[§] Netherlands Organization for Scientific Research.
[⊥] University of Durham.
[#] University of Groningen.

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tion of $PANI(CSA)_{0.5}(Hres)_y$ and phase behavior by small- and wide-angle X-ray scattering (SAXS and WAXS) and electrical conductivity.

Experimental Section

Materials. High molecular weight polyaniline was polymerized at 248 K and reduced to emeraldine base, using methods reported in detail elsewhere.[31] The synthesis yields relatively high molecular weight with $M_w = 265\,000$ g/mol. Camphorsulfonic acid (CSA) was purchased from Acros, 4-hexylresorcinol (Hres) from Fluka, and formic acid from Riedel-de-Haën. CSA, Hres, and formic acid were of purity of 98% and were used without further purification.

Sample Preparation. PANI and Hres were first dried in a vacuum ($<10^{-2}$ mbar) at 25 °C for at least 24 h. A relatively low drying temperature of emeraldine base was selected to reduce the danger of cross-linking. $PANI(CSA)_{0.5}(Hres)_y$ complexes were prepared from formic acid solution where the amount of CSA corresponds to the nominally stoichiometric protonation of the iminic nitrogens, and $y = 0$, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 denotes the number of Hres groups per aniline repeat unit. PANI was slowly added in formic acid, and a concentration less than 0.5 wt % was used. The mixture was magnetically stirred for 9 days at room temperature. Optical microscopy suggested almost total solubility of PANI in formic acid. The minor insoluble fraction of PANI was filtered off by using Millipore Durapore filters (in the order 10, 5, 1.2, 0.45, and 0.22 μm), and the insoluble fraction turned out to be only 1.4 wt % of the initial amount of PANI added. CSA was added to the PANI/formic acid solution, and the solution was stirred for 3 days. The protonation by CSA is expected to take place because CSA is much stronger acid than formic acid, which is not capable of substantial protonation.[32] The mixture remained clear. Next Hres was added, and the solutions remained clear. Note that at this stage the mixture was stirred only for 15 min, because Hres may react with formic acid upon extended mixing. Finally, formic acid was evaporated at 40 °C, and the samples were subsequently dried in a vacuum oven (10^{-2} mbar) at 50 °C for 30 min. A short drying time was used because almost all formic acid evaporates already at room temperature and to prevent evaporation of Hres. This low temperature also ensures that no CSA degrades during extended drying.

Small-Angle X-ray Scattering (SAXS). The samples were pressed between two polyimide films. The SAXS measurements were performed at the Dutch-Belgian beamline (BM26) of European Synchrotron Radiation Facility in Grenoble, using a beam of 16 keV with an area of 0.35×0.5 mm^2 at the sample position. The SAXS data were collected with a two-dimensional wire chamber camera at a distance of 1.8 m from the sample. A description of beamline is given elsewhere.[33] Samples were heated from room temperature to 105 °C, i.e., above the melting point of Hres. Subsequently, samples were cooled back to room temperature.

Additional measurements were performed using a sealed fine focus Cu X-ray tube in a point-focus mode. The Cu Kα ($\lambda = 1.542$ Å) radiation is monochromatized with a Ni filter and a totally reflecting glass block (Huber small angle chamber 701). Scattered radiation was detected by a one-dimensional proportional counter (MBraun OED-50M). Detailed information is given elsewhere.[19]

Wide-Angle X-ray Scattering (WAXS). WAXS experiments were carried out with Cu Kα radiation, monochromatized by a quartz monochromator in the incident beam, using the diffractometer in the symmetrical transmission mode.

Conductivity. Thin films were cast from formic acid on a glass plate with gold electrodes evaporated onto the plate. Conductivity was measured using a Keithley 2400 source measure instrument and a four-point geometry constant current method.

Results and Discussion

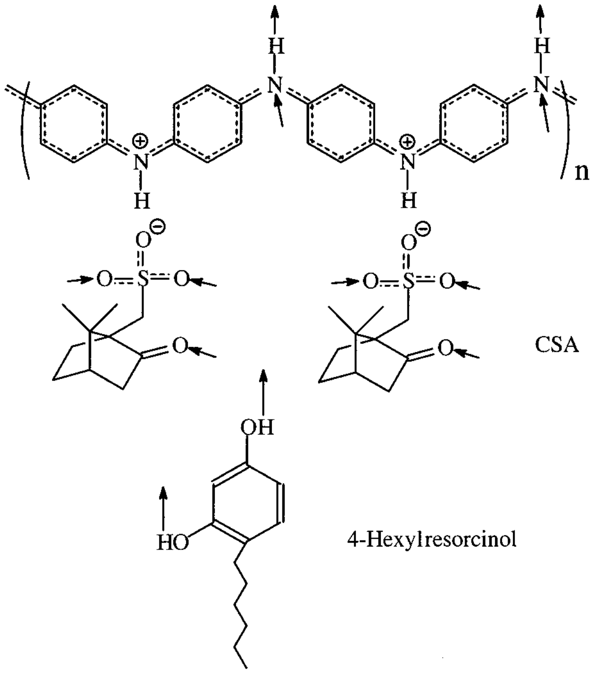

Figure 1. Polyaniline (PANI), camphorsulfonic acid (CSA), and 4-hexylresorcinol (Hres). The iminic nitrogens of PANI are protonated to nominally allow $PANI(CSA)_{0.5}$. The different hydrogen bonding sites are denoted by arrows.

We will first discuss formation of the complexes between PANI, CSA, and Hres. That the protonation of the iminic nitrogen sites of polyaniline emeraldine base due to CSA takes place in different solvents is well established using UV/vis spectroscopy and will not be addressed here in any further detail.[29,34,35] The resulting complex will be denoted as $PANI(CSA)_{0.5}$ according to the nominal composition. The suggested hydrogen bonding between $PANI(CSA)_{0.5}$ and 4-hexylresorcinol, and especially the hydrogen bonding sites, are more difficult to study. Self-organized hydrogen bonded complexes between poly(4-vinylpyridine) and alkylphenols have been studied in detail previously.[19] In this case, the hydrogen bonding acceptors and donors are the pyridine amines and the phenolic hydroxyls, respectively, which allow detailed identification of the hydrogen bonding using FTIR. In a close analogy with the present work, self-organization has also been observed in supramolecules consisting poly(4-vinylpyridinium methanesulfonate) hydrogen bonded to alkylphenols.[3,36] In this case the hydrogen bonding probably takes place between the oxygen of the sulfonate group (acceptor) and phenolic hydroxyl group (donor). However, due to the complicated FTIR bands of the sulfonate groups, the bonding has not yet been directly verified. The same complication arises in the present case where the possible hydrogen bonding acceptors are the oxygens of the sulfonates, the amines of PANI, and the carbonyl group of CSA, whereas the hydrogen bonding donors are the two hydroxyl groups of Hres as well as the amines of PANI. The potential hydrogen bonding sites have been indicated in Figure 1. Note that not even hydrogen bonding to the carbonyl groups can be unambiguously interpreted using FTIR because both the amines of PANI and hydroxyls of Hres can hydrogen bond to it. Therefore, the FTIR spectra are not presented here. However, indirect effects of hydrogen bonding between $PANI(CSA)_{0.5}$ and Hres can be studied: At the resolution of optical microscopy, the films of $PANI(CSA)_{0.5}(Hres)_y$ cast from formic acid were homogeneous, and no evidence of macroscopic phase separation was observed. By contrast, macroscopic phase separation was found if the alkyl chain length is increased or if the number of hydroxyl groups is reduced: for example, pentadecylphenol macroscopically phase separates from PANI(CSA)$_{0.5}$, as the long alkyl chain becomes too repulsive in comparison with the reduced attraction allowed by the single hydrogen bond. Therefore, the self-organized complexes of PANI(CSA)$_{0.5}$ require careful balancing between the attraction and the repulsion. This observation is in accordance to our results with an other rigid conjugated polymer, i.e., poly(*p*-pyridine).[30] Note that in the case of flexible polymers a long alkyl chain and a single hydrogen bond still allows self-organization, such as the stoichiometric complex between poly(4-vinylpyridine methanesulfonate) and pentadecylphenol.[3,36]

In conclusion, the hydrogen bonding between PANI(CSA)$_{0.5}$ and Hres seems plausible, but the exact sites of hydrogen bonds as yet cannot be identified. It would not be surprising if the bonding incorporates molecular recognition, where the two possible hydrogen bonds and a π-stacking between the phenolic ring and the PANI rings would contribute synergistically due to a steric match. A related structure was suggested for PANI(CSA)$_{0.5}$(*m*-cresol)$_{0.5}$ by quantum chemical calculations in which case, due to the very short alkyl chain (methyl) of *m*-cresol, one hydrogen bond suffices to prevent phase separation in combination with π-stacking.[37] Note also that in another study resorcinol was experimentally found to be a solvent for PANI(CSA)$_{0.5}$.[38]

We next consider the structures, as determined using SAXS. Figure 2a shows the scattering intensities at 105 °C for PANI(CSA)$_{0.5}$(Hres)$_y$, with $y = 0.5$, 1.0, 1.5, and 2.0 as well as pure PANI(CSA)$_{0.5}$, i.e., $y = 0$, and Hres. This high temperature was selected as it is above the melting temperature of Hres (65 °C), and thus the tendency for Hres crystallization does not complicate the interpretation. PANI(CSA)$_{0.5}$ has no sharp peaks in the SAXS region. The melt Hres shows a flat peak due to a correlation hole.[39] The samples for $y = 1.0$, 1.5, and 2.0 show three sharp peaks ($1q_1$, $\sqrt{3}q_1$, and $2q_1$), which suggests that PANI(CSA)$_{0.5}$(Hres)$_y$ supramolecules self-organize into a hexagonal cylindrical structure with a distance around 35 Å (Figure 3). In the case $y = 0.5$, there seems to be superimposed a flat correlation holelike peak, possibly due to local fluctuations of the structures. The changes in the distance between the cylinders are quite small upon increased y. Figure 2b shows the SAXS intensity patterns at room temperature before heating to 105 °C. The SAXS data at 25 °C (Figure 2b), after subsequent heating to 105 °C (Figure 2a) and after cooling back to 25 °C, are quite similar, the difference being that the peaks become sharper upon annealing. At a high amount of Hres, i.e., $y = 2.0$, another flat scattering peak is observed around 0.3 Å^{-1} in Figure 2b, probably because some Hres may have a tendency to phase separate.

Figure 4 shows the WAXS intensities of PANI(CSA)$_{0.5}$, PANI(CSA)$_{0.5}$(Hres)$_{1.0}$, and Hres. The intensity curve of PANI(CSA)$_{0.5}$(Hres)$_{1.0}$ does not include any features of the crystalline Hres. In the case of PANI(CSA)$_{0.5}$(Hres)$_y$, the formation of the supramolecules due to the hydrogen bonds between Hres and PANI(CSA)$_{0.5}$ disturbs crystallization, and there are too few PANI chains within each cylinder to render crystalline peaks in WAXS.

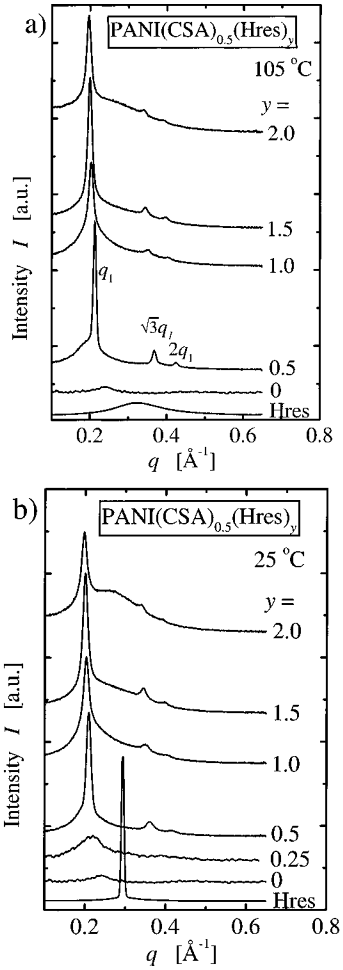

Figure 2. SAXS patterns of PANI(CSA)$_{0.5}$(Hres)$_y$ complexes ($y = 0$, 0.25, 0.5, 1.0, 1.5, and 2.0) and Hres (a) at 105 °C and (b) at 25 °C before the heating to 105 °C, indicating the extent of annealing to the peaks. The peaks at $1q_1$, $\sqrt{3}q_1$, and $2q_1$ are characteristic for hexagonal cylindrical structures.

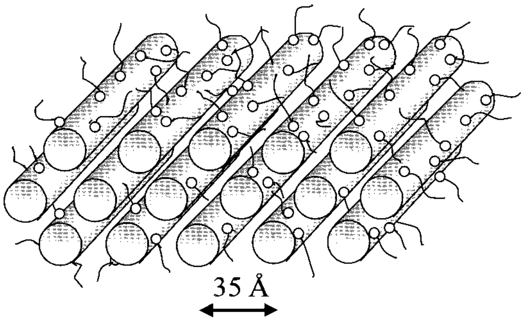

Figure 3. Proposed scheme of the self-organized cylindrical structure where the cylinders contain PANI(CSA)$_{0.5}$ chains and the phenolic groups of the 4-hexylresorcinol molecules. The hexyl tails microphase separate from the cylinders.

PANI(CSA)$_{0.5}$ film cast from formic acid shows conductivity of ca. 5×10^{-3} S/cm. This relatively low conductivity agrees with earlier studies in which low conductivity is observed when relatively poor solvents, such as chloroform or formic acid, are used.[34,40] In such cases, PANI(CSA)$_{0.5}$ forms "compact" coils which limits charge delocalization and interchain charge transport. Casting from a better solvent, such as *m*-cresol, causes more open coils, thus leading to more than 4 orders of magnitude increase in conductivity.[40,41] Further, orientation of PANI processed from good solvents yields

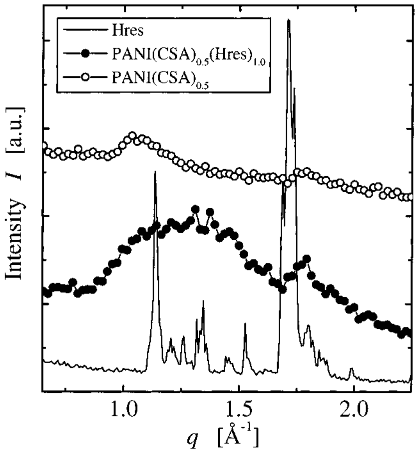

Figure 4. WAXS intensity patterns of PANI(CSA)$_{0.5}$, PANI-(CSA)$_{0.5}$(Hres)$_{1.0}$, and Hres cast from formic acid. Note that in this case even PANI(CSA)$_{0.5}$ is essentially amorphous due to the rapid evaporation of formic acid in comparison to *m*-cresol, which allows high crystallinity.

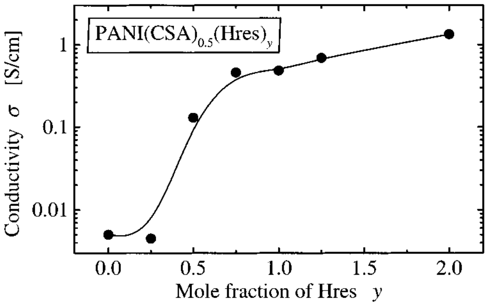

Figure 5. Dc conductivity of PANI(CSA)$_{0.5}$(Hres)$_y$ complexes as a function of a mole fraction of Hres. Disordered structure is observed for $y = 0$ and 0.25 whereas cylindrical self-organization for $y = 0.5$, 1.0, 1.25, and 2.0.

higher conductivities still[42] as does orientation of PANI fibers formed by wet spinning.[31] In the present case a low conductivity is obtained even for $y = 0.25$, in which case the structure is disordered, based on SAXS (see Figure 2b). Interestingly, the conductivity increases 2 orders of magnitude as the cylindrical self-organization is achieved. This correlation between structure and conductivity suggests that upon formation of the self-organized structures the PANI(CSA)$_{0.5}$ chains take up a more elongated conformation upon the suggested confinement in the cylinders.

Conclusions

In this paper we demonstrate that PANI(CSA)$_{0.5}$-(Hres)$_y$ supramolecules self-organize into hexagonal cylindrical structures, if more than ca. 0.5 mol of Hres vs moles of aniline repeat unit is hydrogen bonded to PANI(CSA)$_{0.5}$. Therefore, conducting cylindrical nanoscale wires of polyaniline can be easily prepared. The concept relies on the following findings: Low-temperature polymerization of PANI[31] allows high solubility in formic acid to prepare the supramolecules, hexylresorcinol provides the balance between attraction and repulsion, and CSA and PANI provide potential hydrogen bonding acceptor sites. The conductivity of PANI-(CSA)$_{0.5}$(Hres)$_y$ complexes increased when the cylindrical structures are formed. This could be due to a more extended conformation of PANI chains upon confinement in the cylinders.

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