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ORIGINAL CONTRIBUTION

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# Polypyrrole tubes via casting of pyrrole-$\beta$-naphthalenesulfonic acid rods

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**Abstract** A comprehensive study gives experimental evidence that a complex made from pyrrole and $\beta$-naphthalenesulfonic acid in a molar composition of 3:1 acts as morphological precursor in the subsequent oxidative polymerization of pyrrole initiated with ammonium peroxodisulfate. The precursor complex itself is unable to polymerize but its outer parallelepipedal shape with a high aspect ratio is templated in the inner surface of the formed conducting polypyrrole tubes.

**Keywords** Polypyrrole · Oxidative polymerization · $\beta$-Naphthalenesulfonic acid · Complex formation

## Introduction

Conducting polymers promise a variety of potential applications such as materials for biosensors, microactuators, or antistatic coatings [1]. Among intrinsic conducting polymers with conjugated double bonds polypyrrole is of special interest because of its high stability against ageing of both its conductivity and its mechanical properties [2].

The oxidative coupling polymerization of pyrrole (PY) in aqueous media in the presence of $\beta$-naphthalenesulfonic acid (NSA) as dopant and ammonium peroxodisulfate (APS) as oxidant yields, within certain concentration ranges of PY and NSA, conducting polypyrrole (PPY) with tubular or fibrillar morphology, as has been known since the pioneering work of the group of M. Wan [3, 4, 5, 6, 7]. Despite all the papers published so far the mechanism of the formation of these PPY-tubes is still not clear, as there is more speculation than proven experimental facts. However, the situation seems to be similar to the polymerization of aniline, in which a polymer with comparable morphology was obtained and experimental evidence was given that a complex between the monomer and the NSA might act as in-situ formed template during the subsequent polymerization [6, 8]. Particularly in these papers all conclusion drawn concerning the behavior of PY are based on experiments with aniline and no experimental data are available proving directly complex formation between PY and NSA. On the contrary, the authors deny complex formation due to acid–base interactions in that case [6]. Instead the authors propose micelles of NSA swollen with PY, for which again no experimental evidence is given and which again are not confirmed by other publications [7]. To the best of our knowledge there is only one publication describing investigation of micelle formation by NSA [9] with the Archibald ultracentrifugal method. The authors were able to show that NSA does not form micelles whereas NSA–formaldehyde condensates do. On the other hand there are experimental data available showing that NSA is able to reduce the surface tension of aqueous solutions [10]. For example, 0.1 g of NSA per liter water reduce the surface tension of water to a value of 67.9 mN m$^{-1}$.

In general, the reaction under consideration is an interesting example of a special kind of heterophase polymerization [11] as the final state is a dispersion of PPY in water whereby the initial state is an emulsion of PY in water, although without any surfactant. In this sense interfacial or colloidal effects might be of importance but they are beyond the scope of these particular investigations.

The aim of this contribution is to shed some light on the mechanism of formation of black tubular PPY during oxidative coupling of PY with peroxodisulfate in the presence of NSA. Special emphasis is placed on the interaction between NSA and PY before the oxidant is added. The results obtained clearly prove that before addition of the oxidant NSA and PY interact in aqueous solution and form a complex, which precipitates at temperatures of about 0 °C. Data regarding complex composition and morphology are presented.

## Experimental

### Materials

Pyrrole (Acros) was distilled and stored in a refrigerator until use. $\beta$-Naphthalenesulfonic acid (Acros, melting point 77–79 °C) and ammonium peroxodisulfate (Aldrich) were used as received. For all calculation the molecular weight of $\beta$-naphthalenesulfonic acid was assumed to be 262.28 g mol$^{-1}$, which corresponds to the trihydrate, $C_{10}H_7SO_3H \cdot 3H_2O$ [12]. The water was taken from a Seral purification system (Purelab Plus) with a conductivity of about 0.06 $\mu$S cm$^{-1}$ and used without any further treatment.

Elemental analysis for C, H, N, S was carried out with a vario EL elemental analyzer (Analysensysteme, Hanau, Germany).

### Methods

Transmission electron microscopy (TEM) was performed with a Zeiss EM 912 Omega microscope operating at 100 kV. Thin sections were prepared with an ultracut (Leica) from samples embedded in an acrylic resin (LR White Resin, medium grade, Plano). Scanning electron microscopy (SEM) pictures were obtained with a Gemini 1550 scanning electron microscope (Leo). Light microscopy (LM) images were taken with a Olympus BX50 microscope equipped with a CCD camera.

Fourier-transformed infrared (FTIR) spectra of the solid materials and of the monomer were recorded with an Impact 400 spectrometer (Nicolet, USA) in a KBr pellet (2 mg of sample in 200 mg KBr) and with an FTS 6000 spectrometer (BioRad) in attenuated total reflection mode with a golden gate diamond unit (Specac), respectively.

Size-exclusion chromatography (SEC) was performed with standard equipment in *N*-methylpyrrolidone at 70 °C with refractive index detection (Showdex RI-71) according to standard procedures. A column set was employed consisting of two polystyrene gel columns 5 µm and 8×30 mm (PSS-gel 1000 Å and PL-gel 100 Å).

The powder diffraction pattern was recorded in transmission geometry with a computer controlled goniometer (HZG-4, Freiburger Prätzisionsmechanik) with proportional counter. Nickel-filtered copper radiation ($\lambda = 0.154$ nm) of a sealed fine-focus X-ray tube was collimated by slit systems both in the incident and the reflected beam resulting in an instrumental resolution of about 0.04°.

The electrical conductivity was determined by the so-called "four-point method" from specimens of the solid materials with known geometry, which were formed from powders at a pressure of about 10 tons. Stainless steel tips were used for the measurements and gold contacts for closing the current loop. Voltage and current were measured with multimeters (Metrohit S16). The data were transferred to a computer and evaluated with special registration software.

### Reactions

The results described by Wan et al. [3] were the starting point for own investigations on the preparation of black conducting PPY tubes. In principle, it was possible to repeat the experiments described above although the particular concentration ratios between NSA, PY, APS, and water had to be changed in order to obtain tubular conducting PPY reproducibly with different overall reaction volumes and in different reactors. In particular, the differences in the ratio of recipe components as summarized in Table 1 show that the reactant concentrations relative to the mass of water had to be increased compared with the procedure given in Ref. [3].

It is necessary to point out also, in accordance with the results of Wan et al., that for the given recipe components (NSA, PY, APS) a necessary prerequisite to obtain exclusively PPY tubes is to carry out the oxidative coupling at lower temperatures by placing the reaction vial in an ice-bath (about 0 °C). At higher temperatures mainly granular PPY is formed although in some experiments a few tubes were found to coexist with mainly PPY grains.

**Table 1** Reaction conditions leading to tubular conducting PPY

| Reactant ratio | Wan et al. [3] | This work |
|---|---|---|
| NSA ($g/g_{\text{water}}$) | 0.1040 | 0.2353 |
| PY ($g/g_{\text{water}}$) | 0.0333 | 0.0588 |
| APS ($g/g_{\text{water}}$) | 0.0213 | 0.0588 |

All reactions were carried out in glass vials with an overall volume between 15 and 20 mL and an inner diameter of about 2.5 cm with magnetic stirring in a fume cupboard in a laboratory atmosphere.

For the oxidative coupling reactions the complex was not isolated but 0.2 g APS dissolved in 1 mL of water was slowly added to the dispersion of the complex, which has a color between light brown and gray. The mixture was allowed to react for 1 hour during which its color changed to black. The polymer was then separated from the continuous phase by filtration, washed with water and ethanol, and finally dried under vacuum at room temperature for at least 24 hours. The polymerization yield relative to the initial mass of PY is about 50%.

Separate synthesis of the complex between PY and NSA was carried out as follows. PY (0.2 mL) was added to solutions of different amounts of NSA (0.8 g in 2.4 mL water was the standard concentration as also used for polymerization) with magnetic stirring. After 5 minutes at room temperature the mixture was placed in an ice bath where after a certain period of time the complex precipitated. Stirring was continued for about 5 minutes and then the complex was separated from the continuous phase by filtration and carefully washed with water. The complex was then dried in vacuum for more than 24 hours. The yield of the complex relative to the initial mass of PY was about 15%. The melting point of the complex was between 94 and 96 °C.

## Results and discussion

The SEM photographs at various magnifications shown in Fig. 1 illustrate typical morphological features of the PPY tubes prepared under the given experimental conditions. At the lowest magnification (Fig. 1a) the polymer appears as an irregular pile of stiff rods. These rods can be as long as almost 50 μm whereas their diameter is up to about 5 μm. It should be emphasized that PPY is very brittle and hence these rods are very probably broken due to mechanical stress during handling after their preparation. Increasing magnification as from Fig. 1b to 1d reveals that the surface of these rods is not smooth but is coated with fibrillas of different thicknesses. The thinnest fibers have a diameter lower than 20 nm, as can be deduced from Fig. 1d. Figure 1c shows a broken rod and reveals that the PPY rods are hollow inside.

TEM pictures of microtomed cross sections as depicted in Fig. 2 confirm that the PPY rods are elongated hollow objects (overview photograph in Fig. 2a). The magnified picture (Fig. 2b) shows that both the internal and the external shapes are irregular, occasionally with sharp edges and kinks. However, the internal shape looks in any case rhombus- or parallelogram-like. Moreover the internal surface appears smooth whereas the external is not, as already seen from the SEM images. The wall thickness is up to 500 nm.

These experimental findings are really surprising and immediately lead to questions concerning the mechanism of formation of these tubular morphologies with polydisperse cavities and regions in the wall, especially the inner wall, with high curvature, because the PPY is a brittle and rather non-flexible polymer [13]. The formation of the morphologies shown in Figs. 1 and 2 requires either flexible polymer chains or low-molecular-weight species.

A closer look at the reaction mixture during the early stages revealed an astonishing result. When the reaction mixture consisting of PY and NSA, which at room temperature is a brownish but transparent solution, is placed in the ice bath it becomes turbid and a precipitate is formed, which can be easily separated by filtration. Once formed the precipitate is insoluble in water even at room temperature. It must be emphasized that the precipitate is formed in the absence of the oxidant. Elemental analysis of the precipitate after careful washing with water reveals that it is a complex consisting of NSA and PY. The complex is light gray in color and insoluble in water but soluble in polar solvents such as ethanol or *N*-methylpyrrolidone. In contrast with the findings of Wan et al. [6], NSA and PY are also able to form a complex, as was observed until now only for aniline [6, 8]. However, manifestation of the complex as a precipitate requires, under the experimental conditions chosen, temperatures of about 0 °C. The different melting points of the complex and the NSA (94–96 °C and 77–79 °C, respectively) prove that the complex really is a new chemical species. Furthermore, a comprehensive study showed that formation of the precipitate has all the features of a classical nucleation process, for example scatter of the incubation times (i.e. a time lag between placing the mixture in the ice bath and observation of the precipitate) and the possibility of inducing precipitation by addition of a few seed crystals such as NSA. Typical LM images of the precipitate shown in Fig. 3 illustrate the surprising similarity to the morphology of the final PPY.

The PY–NSA complex dispersion consists of stiff rods with considerable polydispersity in their longest dimension, which can be as long as more than 100 μm. SEM pictures of the complex at low magnification (not

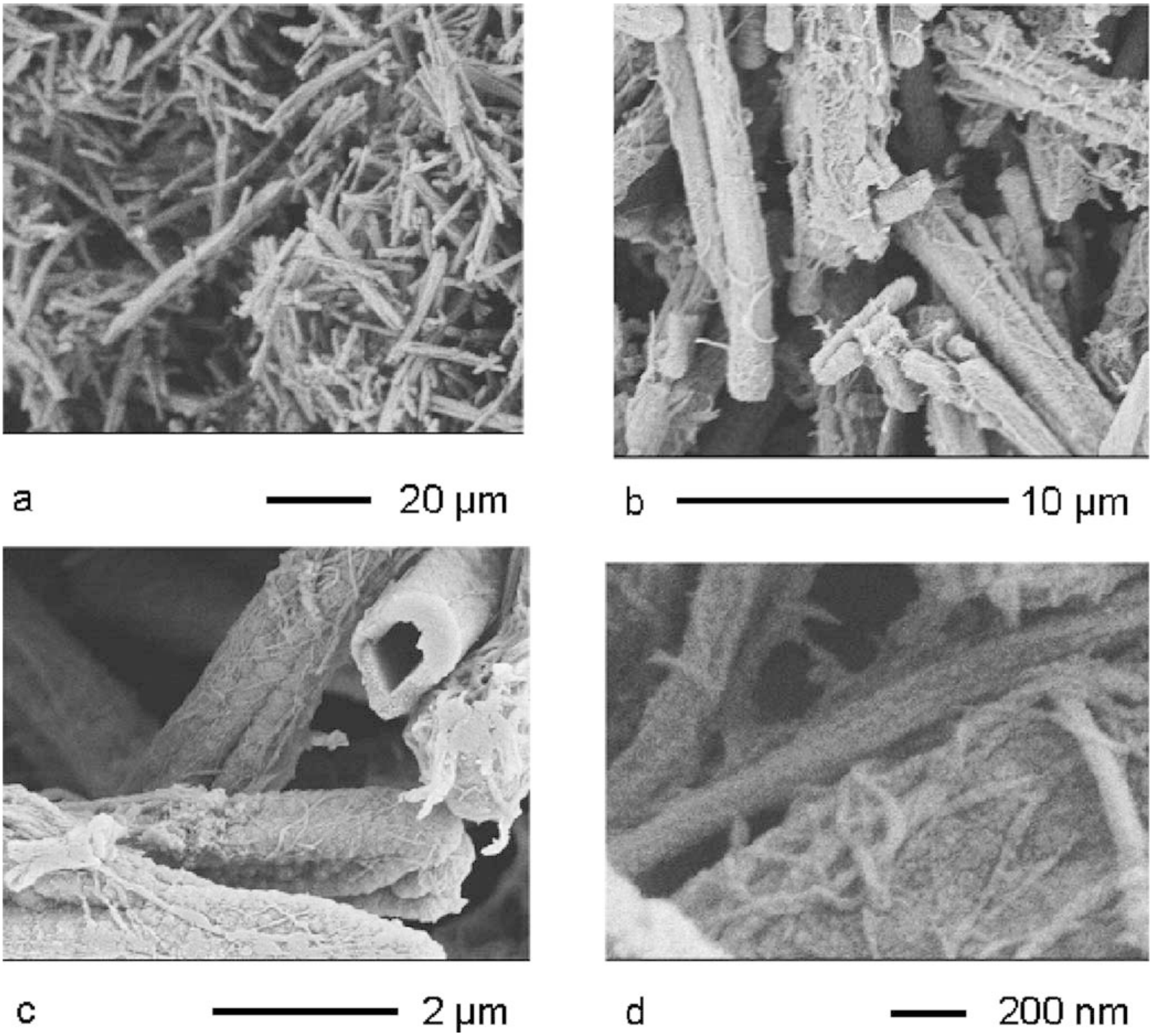


**Fig. 1** SEM photographs showing the morphology of the black PPY powder

shown here) confirm on the one hand the conclusion from LM regarding the complex morphology and on the other hand prove that the handling of the sample (washing, drying, sample preparation for SEM) leads to damage of the virgin morphology. At higher magnification this damage is clearly visible (cf. Fig. 4). The complex appears very brittle as smaller pieces exist beside larger ones and especially the ends of the rods resemble fractured surfaces.

It should be mentioned that the dimensions (height and diameter) of the complex rods are of similar order as those of the final polymer bars. However, in contrast with the PPY rods the surface of the complex particles appears much smoother and less structured. Another characteristic feature of the surface of both the original complex rods and the split pieces are sharp edges (regions of high curvature) and their almost rectangular shape. In contrast, the outer shape of the polymer rods is more round (cf. Figs. 1b–1d). From cross sections of microtomed embedded PY–NSA complex rods, as shown, for example, in Fig. 5, the conclusion can be drawn that these rods also have hollow morphology, because the remaining, non-dissolved material is assembled not in solid shapes but only in wall-like structures. Furthermore, these images prove that the complex is not a polymeric material, because the rods partly dissolve in the acrylate monomer mixture em-

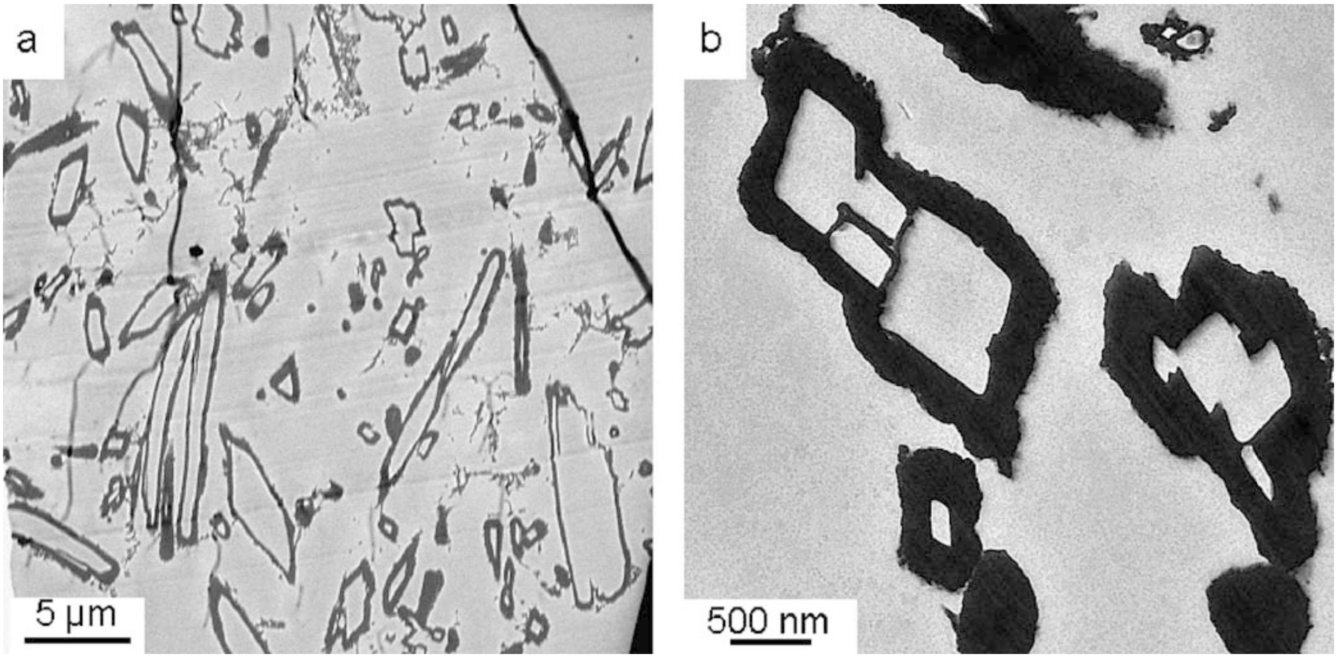


**Fig. 2** TEM photographs of microtomed cross-sections of PPY tubes showing their internal and external surface structure

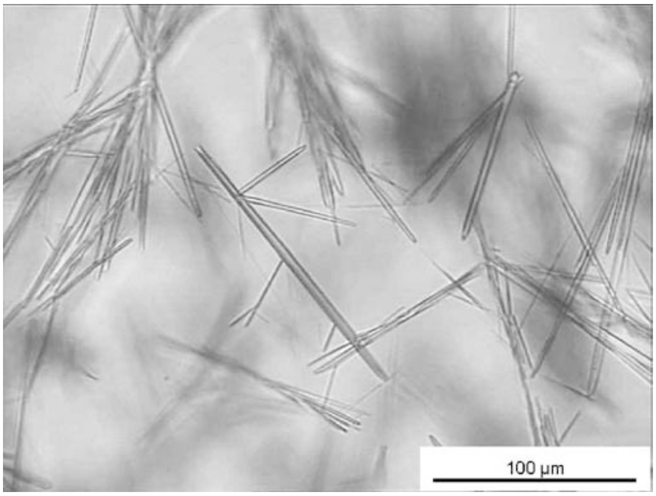


**Fig. 3** LM image of the PY–NSA complex dispersion

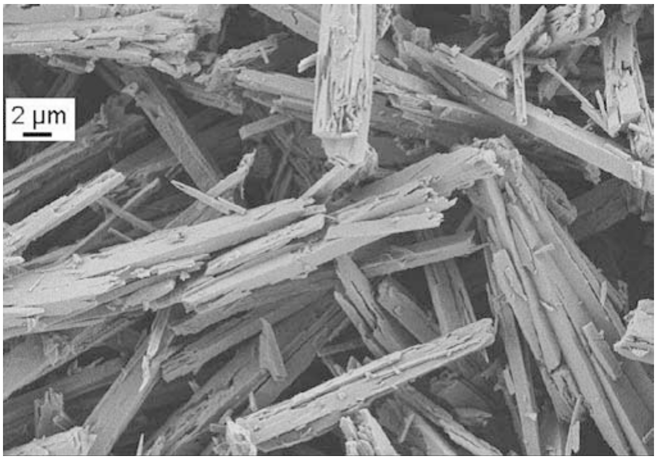


**Fig. 4** SEM photographs of the PY–NSA complex after washing

ployed for the embedding. The interaction with the monomer causes relaxation of the stresses in the complex and hence, the sharp edges disappear (decrease of curvature). So, direct conclusions regarding the shape of the inner surfaces of the PY–NSA complex rods are not possible but it is very likely that the inner surface is as smooth as the outer (cf. Fig. 4).

Precipitation of the complex rods takes place only over a certain concentration range of NSA as illustrated by the data summarized in Table 2.

A large excess of PY prevents precipitation, because of increased solubility of the complex in the continuous phase. In separate experiments it was proven that the complex is soluble in pure PY. At low PY content the complex concentration is obviously not high enough to surmount the precipitation barrier. If precipitation of the complex between PY and NSA happens its shape is always as depicted in Figs. 3–5 as no other morphology has been observed. Moreover, the composition of the precipitate is independent of the composition of the starting mixture with PY:NSA$\approx$3 (statistically $3.00 \pm 0.15$) according to the data in Table 2. This points clearly to specific interactions between both components.

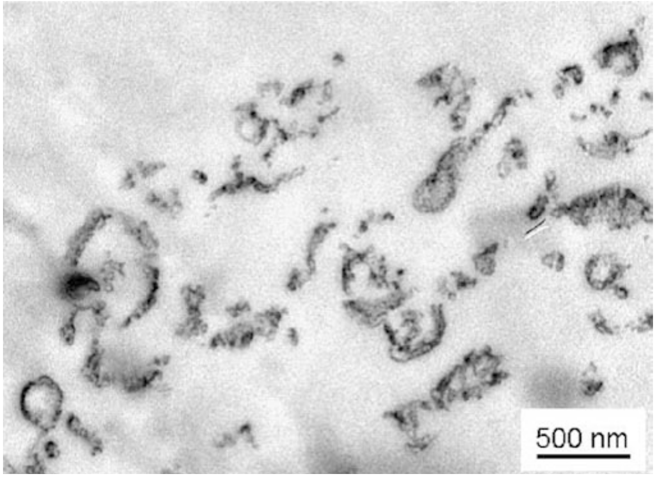


**Fig. 5** TEM photograph of microtomed cross-section of PY–NSA complex rods; the grainy structure is a result of partial dissolution of the complex in the monomer mixture

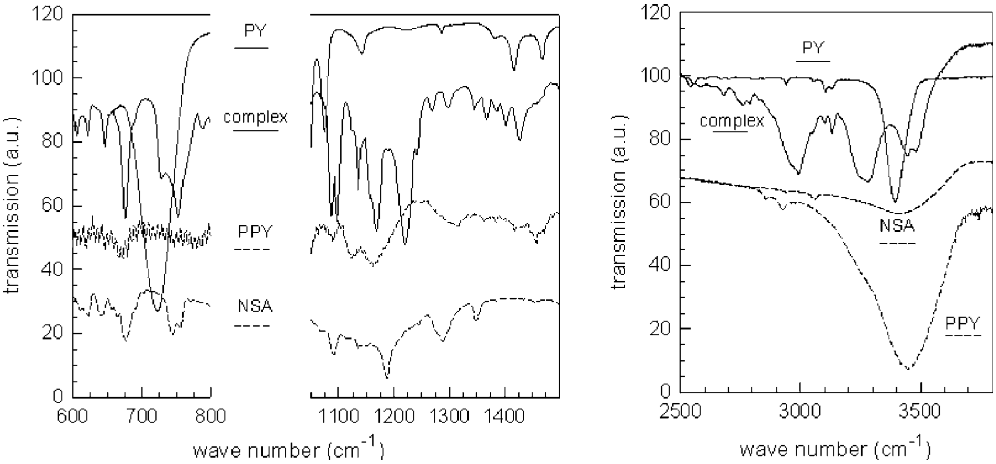
**Table 2** Characterization of PY-NSA complex precipitation[a]

| PY:NSA (starting) | Precipitate | PY:NSA (precipitate) |
|---|---|---|
| 4.64:1 | No | – |
| 1.98:1 | No | – |
| 1.50:1 | Yes | 2.8:1 |
| 1.16:1 | Yes | 3.2:1 |
| 0.94:1 | Yes | 3.1:1 |
| 0.82:1 | Yes | 2.9:1 |
| 0.75:1 | Yes | 3.0:1 |
| 0.55:1 | Yes | 3.0:1 |
| 0.46:1 | Yes | 3.0:1 |
| 0.35:1 | Yes | 2.8:1 |
| 0.23:1 | No | – |

[a] molar ratio of reactants

Indeed the FTIR spectra as put together in Fig. 6 prove the occurrence of specific interactions between PY and NSA; this is apparent from the following changes in the complex spectra compared to those of the individual components. First, the N–H stretching vibration of the PY, which is clearly visible in monomer at 3400 cm$^{-1}$ is completely absent from the complex. Instead of the single band three bands (each of which is a doublet) at 2950/2993, 3240/3281, and 3444/3483 cm$^{-1}$ appear. Second, the ring deformation vibration of the PY monomer at 722 cm$^{-1}$ is also absent from the PY–NSA complex. Moreover some changes are visible in the region of the NSA aromatic ring vibrations between 600 and 800 cm$^{-1}$, especially pertaining the doublet at 744 and 756 cm$^{-1}$ in the pure NSA. Third, in the absorption region of the sulfonic acid group the single absorption band in the NSA at 1090 cm$^{-1}$ splits in the complex into a doublet (1086 and 1097 cm$^{-1}$) and the NSA absorption at 1186 cm$^{-1}$ disappeared and two new bands at 1168 and 1220 cm$^{-1}$ appeared in the complex. Furthermore several new absorptions with lower intensities appear in the complex between 1250 and 1450 cm$^{-1}$. All these results support a structure of the complex between PY and NSA as shown schematically in Fig. 7 with basically three kinds of interaction in which the PY:NSA = 3:1 stoichiometry is proven by the elemental analysis data (cf. Table 2). The first kind of interaction is the acid–base interaction as NSA is a strong acid with a p $K_a$ value of $\sim$0.57 [14] and the NH-group in PY is strongly basic with a p $K_a$ value of 17.5 [13]. This interaction causes the observed changes in the FTIR spectra in the region of the NH and sulfonic acid vibrations. The second kind of interaction might be $\pi$–$\pi$ stacking causing the vanishing of the PY ring deformation vibration and the changes in the absorption of the aromatic vibrations of NSA. Finally, hydrogen bonds between two PY molecules bound via $\pi$–$\pi$ stacking and the non-ionized sulfonate oxygen atoms might contribute to the stability of the PY–NSA complex. A first idea of how the participating molecules might be arranged in the precipitate obeying the 3:1 (PY:NSA) molar ratio is sketched in Fig. 7.

**Fig. 6** FTIR spectra of PY, NSA, the precursor complex, and the PPY



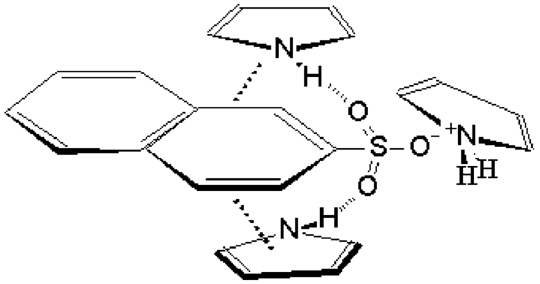


**Fig. 7** Schematic drawing of possible arrangement of PY and NSA in the precipitated complex (not to scale)

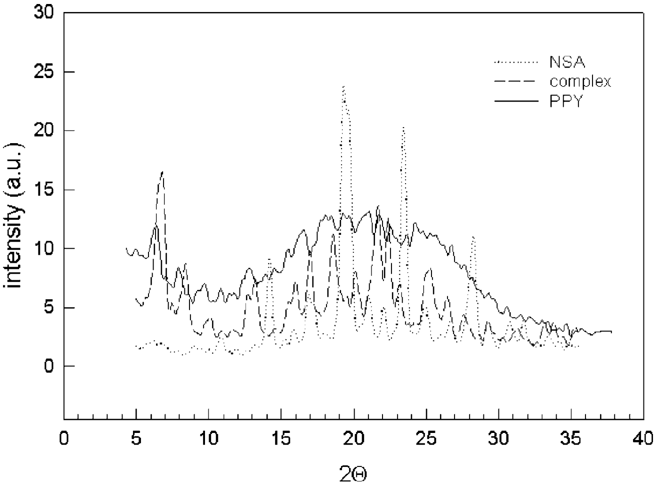


**Fig. 8** X-ray diffraction pattern of NSA, PY–NSA complex, and PPY

Regarding the polymerization mechanism it is important to note that the FTIR results prove a clear difference between PPY and the PY–NSA complex especially in the absorption region of the NH-group, thus indicating that the complex might not act as building block or repeating unit for the polymer. Compared with the monomer the absorption region of the polymer is much broader with a maximum at 3450 $\mathrm{cm}^{-1}$ and a shoulder at about 3250 $\mathrm{cm}^{-1}$. Obviously, the polymer consists of complexed and free PY units. This conclusion is supported by elemental analysis data, because the PY:NSA ratio in the polymer (prepared with different starting ratios of PY to NSA) is larger, although only slightly $3.60 \pm 0.44$, than that of the complex. In similar experiments Wan et al. [6] determined a ratio of $3.39 \pm 0.21$ in the final polymer.

X-ray diffraction data such as presented in Fig. 8 show clear differences between NSA, PY–NSA complex, and PPY.

The crystal structure of NSA is, because of complex formation with PY, completely changed. The complex has reflections at lower values of 2Θ than the neat NSA, indicating complex formation. The peak in the diffractogram of the complex at $2\Theta = 6.8$ leads to a characteristic spacing of about 1.3 nm. Compared with the NSA and the complex the diffractogram of the PPY indicates a much lower degree of crystallinity. However, in the range of 2Θ-values between 6 and 8 two reflexes are clearly visible. These reflexes, which are also present in the complex are in the polymer slightly shifted towards lower 2Θ-values, hence indicating slightly larger spacing (1.38 nm). These data suggest that the polymerization reaction, which takes place via coupling of pyrrole rings in the α-positions and proton abstraction leads to a different molecular arrangement between the NSA molecules and the PY units compared with that of the PY–NSA complex, which is formed by only physical interactions and where the PY molecules can arrange almost independently from each other.

Furthermore, other properties such as the solubilities of the complex and the polymer reveal additional differences between the complex and the PPY. For example, the complex is completely soluble in *N*-methylpyrrolidone and ethanol whereas the polymer is only partly soluble in *N*-methylpyrrolidone and not soluble in ethanol. The SEC obtained in *N*-methylpyrrolidone (cf. Fig. 9) manifests at least two important findings.

First, the soluble portion of the polymer (PPY-s), that is, the low-molecular-weight fraction, elutes in a similar range as the neat complex and a fairly sharp peak at high elution volumes characterizes both chromatograms. Second, the NSA elutes at almost the same position and with the same shape and width as the main portion of the PPY-s whereas the main fraction of the complex elutes at higher volumes. This result proves that the NSA, which is bound to the polymer, is set free in *N*-methylpyrrolidone solution under these particular conditions (70 °C). In contrast with the doped PPY, the binding in the complex

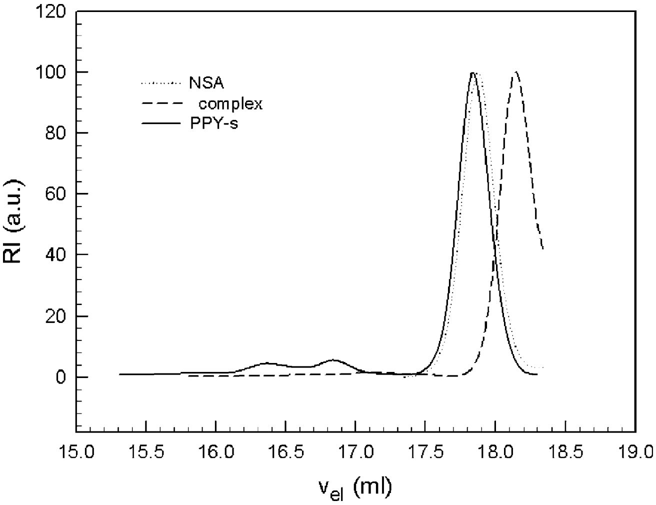


**Fig. 9** SEC traces of NSA, PY–NSA complex, and PPY-s (Note, the PY–NSA complex and the polymer were purified after preparation with water and ethanol, respectively, and hence, the polymer should not contain any complex because it is soluble in ethanol.)

is much stronger as no separate NSA is detected. The stronger binding in the PY–NSA complex was also proven by FTIR spectroscopy. The shift between the pure NSA and the PY–NSA complex indicates that the separation probably takes place not only in the SEC mode but at least partly also due to interactions between the solute and the column material (HPLC mode).

All these data (SEC, X-ray diffraction, FTIR) prove that the cleaning procedure of the reaction product (first washing with water and then with ethanol) was effective as obviously no complex is left in the polymer. Consequently, it might be concluded that all data presented for the polymer are not influenced by impurities arising from starting materials or the complex. This is of special importance for potential applications of the PPY requiring high electrical conductivity, because the complex has a conductivity of only $3.7\times10^{-6}$ S cm$^{-1}$. In contrast, the black PPY has orders of magnitude higher electrical conductivity of about 15 S cm$^{-1}$.

## Conclusions and summary

The experimental results presented lead to the conclusion that PY and NSA spontaneously form a crystalline complex with a molar composition of 3:1 (PY:NSA). The brittle complex precipitates from aqueous solution in a parallelepipedal shape with an aspect ratio up to larger than 10. This complex determines the shape of the final PPY formed during subsequent oxidative polymerization if an excess of PY monomer is present. The monomeric PY bound in the complex cannot be polymerized by addition of oxidant. If a dried, pure complex is re-dispersed in water and oxidant is added no polymerization takes place. If, however, the dried, pure complex is re-dispersed in the mother liquor of a complex polymerization starts after addition of oxidant leading to tubular PPY. These results prove the strong binding between the NSA and the PY monomer in the precursor complex. Another experimental result supporting the idea that the complex governs the morphology of the PPY is the formation of granular PPY if no precipitated precursor complex is present. This was observed if the NSA was added only after the oxidant, if the polymerization was carried out at elevated temperatures where no complex precipitation is observed, or if the polymerization was initiated in the mother liquor.

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