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STRUCTURAL INVESTIGATIONS OF POLYANILINE PREPARED IN THE PRESENCE OF DODECYLBENZENESULFONIC ACID

D. Tsotcheva[1], *T. Tsanov*[1], *L. Terlemezyan*[1] *and S. Vassilev*[2]

[1]Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[2]Central Laboratory of Power Sources, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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Abstract

Structural studies of powdered polyaniline (PANI) prepared in aqueous medium by the oxidative polymerization of aniline in the presence of dodecylbenzenesulfonic acid (DBSA) were performed by means of DSC and WAXS. The influence of the alkyl side-chains on the structure and crystallinity of the as-synthesized PANI–DBSA and on the structural transitions taking place in PANI upon washing and heating were investigated. It was found that DBSA induces crystallinity in the rigid matrix of PANI, and residual crystalline phases were also observed after the deprotonation of PANI–DBSA. For the first time, a melting peak and a relaxation transition of non-cross-linked PANI were registered.

Keywords: crystallinity, differential scanning calorimetry, dodecylbenzenesulfonic acid, melting, polyaniline, relaxation transitions, wide-angle X-ray scattering

Introduction

It was recently reported that, through protonation with functionalised acids such as dodecylbenzenesulfonic acid (DBSA), polyaniline (PANI) can be transformed into its conducting form (PANI–DBSA complex), which can be ‘dissolved’ (the precise term should be dispersed) in many common non-polar or weakly polar organic solvents [1–5]. On the other hand, the long alkyl side-chain of DBSA makes PANI compatible with bulk polymers of similar molecular structure (e.g. polyolefins) and facilitates its processing by conventional techniques, acting as a plasticizer [3, 6–8].

PANI–DBSA complexes obtained by various techniques exhibit different structures [1, 2, 9–12]. To date, predominantly the structures of PANI–DBSA complexes prepared by the protonation of preliminarily synthesized polyaniline-emeraldine base (PANI–EB) with DBSA have been studied. It has been found [9] that electroactive complexes of PANI–EB and DBSA (or another acid with a long alkyl tail) obtained by mixing in the solid state exhibit a well-organized layered structure. Cao *et al*. have reported a PANI–EB protonated with DBSA in ‘solution’ (the precise term should be

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dispersion) [1, 10]. They observed two basic conformations of the PANI–DBSA complex in solution, and two corresponding crystalline forms in the solid state, which are responsible for the polymer conductivity. PANI–EB thermally doped with DBSA has been found to form a liquid-crystalline structure [11].

On the other hand, Osterholm *et al.* [2] have reported a direct, one-step preparation of electrically conducting PANI–DBSA complexes with a unique fibrillar morphology by the emulsion polymerization of aniline in non-polar or weakly polar organic solvents in the presence of DBSA. The fibrillar particles detected by transmission electron microscopy and electron diffraction studies exhibited an exceptional degree of crystalline order and orientation of the PANI chain molecules along the long axis of the fibrils.

There have also been noteworthy structural studies of N-alkylated polyanilines, i.e. PANI derivatives with various alkyl side-chain substituents covalently bonded to the PANI chains, in contrast with the PANI complexes. It has been shown that these polymers exhibit interesting thermal and morphological properties in the bulk state because of their layered structure [12]. The rigid main chains are packed into plate-like layers, and the alkyl side-chains are arranged between the layers, forming paraffinic crystallites.

We recently reported the preparation of a colloidal PANI dispersion via the oxidative polymerization of aniline in the presence of DBSA in aqueous medium [13]. Structural studies of the isolated powdered PANI–DBSA complex obtained by this novel route are presented for the first time in the present article. By using differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS), we set out to establish the influence of the long alkyl side-chain in DBSA on the structure and crystallinity of the as-synthesized PANI–DBSA complex, and also on the structural transitions taking place in PANI on washing and heating (when cross-linking too occurs).

Experimental

PANI–DBSA powder was synthesized by the oxidative polymerization of aniline in aqueous medium, using ammonium peroxydisulfate as oxidant and DBSA according to the procedure describing by Gospodinova *et al*. [13]. PANI–HCl was prepared according to the technique given in [14].

Emeraldine bases (PANI–DBSA–EB and PANI–HCl–EB) were prepared by treating the powdered salts with a dilute (2%) solution of sodium hydroxide.

The thermal transitions of the polymers were determined by using a Perkin Elmer DSC 7 differential scanning calorimeter with a cooling unit in argon atmosphere in the temperature range –60–350°C. A heating rate of 10 and a cooling rate of 200°C min^{-1} were used in the heating and cooling cycles; the transition temperature was reproducible to 2°C. The instrument was calibrated with indium and lead as standards. Samples of about 10 mg were sealed in standard aluminum pans with holes.

Mass losses were determined by weighing the sample pans prior to and after the heating run from ambient temperature (AT) up to 170°C in the calorimetric chamber, according to the equation 100 $(W_1-W_2)/W_1$, where W_1 and W_2 are the sample masses before and after the experiment.

A Philips APD 15 X-ray generator was used for the wide-angle X-ray diffraction experiments. The point focus beam was monochromatized to CuK_α with a graphite crystal. The X-ray source utilized a CuK_α target (l_K=1.54178 Å) with generator settings of 40 kV and 30 mA. The 2θ step size for each individual data collection point was set to 0.025° and the time for remaining on each point was limited to 1 s.

Results and discussion

The X-ray diffraction pattern for PANI–DBSA (Fig. 1, trace 1) shows a number of narrow sharp reflection peaks. After the conversion of PANI–DBSA into PANI–EB (PANI–DBSA–EB), a broad diffuse peak centered at $2\theta\approx20°$ and three overlapping sharp peaks at $2\theta\approx15$, 19 and 24° are observed (Fig. 1, trace 2).

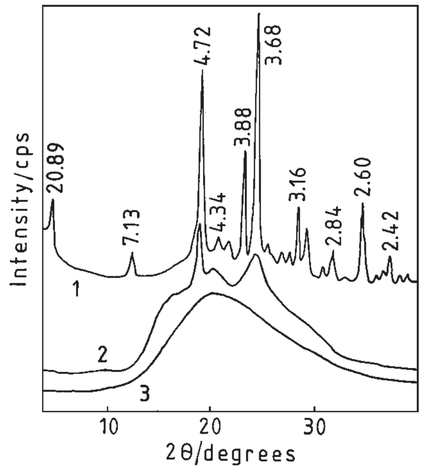


Fig. 1 X-ray diffraction patterns of 1 – PANI–DBSA; 2 – PANI–DBSA–EB; 3 – PANI–HCl–EB

As compared to PANI–DBSA, the intensities of these three peaks are strongly reduced on account of the intensity of the broad peak, associated with scattering from the disordered chains. We assume that the sharp peak at $2\theta=19°$ is due to residual ordered DBSA macromolecules which were not neutralized by NaOH solution because of the hindered diffusion in the solid PANI–DBSA complex. We further consider that the peaks at $2\theta\approx15$ and 24° are related to the DBSA-induced ordering of the rigid PANI main chains, as described below. We used the areas under the crystalline peaks and the amorphous halo of the angular intensity profile to estimate the percentage crystallinity of the polymer systems, according to the equation given in [15]. It is seen that the degree of crystallinity decreases from 68% (as-synthesized PANI–DBSA) to 18% (PANI–DBSA–EB). Figure 1 also depicts the X-ray diffraction pattern of PANI–EB obtained by the deprotonation of PANI synthesized in the presence of HCl

(PANI–HCl–EB) (trace 3), where only a broad amorphous halo at around $2\theta=20°$ is observed, with no discernible order. Obviously, as concerns the two base forms of PANI, only PANI–DBSA–EB exhibits crystalline order. The Bragg interlayer *d* spacings of the polyanilines studied in the present work are presented in Table 1, together with data to be found in the literature ([9, 12, 16–18]. Some of the *d* spacings (3.53, 3.27, 2.91, 2.84, 2.47 and 2.42 Å) of PANI–DBSA coincide with the corresponding spacings of PANI–HCl, investigated by Pouget *et al.* [16]. Some of them (2.84, 2.60 and 2.42 Å) are also similar to those registered for PANI–sodium dodecylsulfate [18]. Since the narrow peaks are presumed to be specific for an anionic lattice [19], they can be assigned to scattering from a lattice built up from main PANI chains and DBSA counteranions. On the other hand, the interlayer *d* spacings of PANI–DBSA (3.37, 3.16, 3.07 and 2.60 Å) which differ from those of PANI–HCl [16] can be related to the ordering of the flexible C_{12}-alkyl chains in the paraffinic crystallites. This assumption is supported by the literature data [9, 12, 18].

Table 1 Bragg *d* spacings of some polyanilines, Å

PANI–DBSA	PANI–DBSA–EB	PANI–HCl–EB	PANI–HCl [16]	PANI–HCl–EB [17]	PANI–Na-dodecyl-sulfate [18]	PANI–EB+DBSA [9]	N-alkylated PANI [12]
20.89	–	–	–	–	–	31.20	26.00
7.13	5.90	–	9.57	–	–	–	–
4.72	4.73	–	5.94	–	–	–	–
4.34	4.35*	4.35*	4.26	4.26*	–	4.30*	4.30*
4.17	–	–	–	–	–	–	–
3.88	–	–	–	–	3.91	–	–
3.68	3.69	–	–	–	3.77	–	–
3.53	–	–	3.51	–	3.45	–	–
3.37	–	–	–	–	–	–	–
3.27	–	–	3.28	–	–	–	–
3.16	–	–	–	–	–	–	–
3.07	–	–	–	–	–	–	–
2.91	–	–	2.98	–	–	–	–
2.84	–	–	2.85	–	2.80	–	–
2.60	–	–	–	–	2.63	–	–
2.47	–	–	2.47	–	–	–	–
2.42	–	–	2.34	–	2.37	–	–

* – amorphous halo

It has recently been found that the WAXS diffraction patterns of N-alkylated polyanilines [12] and electroactive complexes of PANI and DBSA prepared by mixing in the solid state [9] are characterized by only two major reflection peaks. One sharp narrow peak at small angles (*d*=26–31 Å) originates from the distance between the main chains of the polymer in the planes of its layered structure. The other large broad peak at wide angle (*d*=4.3 Å) is a result of a random displacement of the polymer main chains and possible disordering of the alkyl side-chains. We consider that

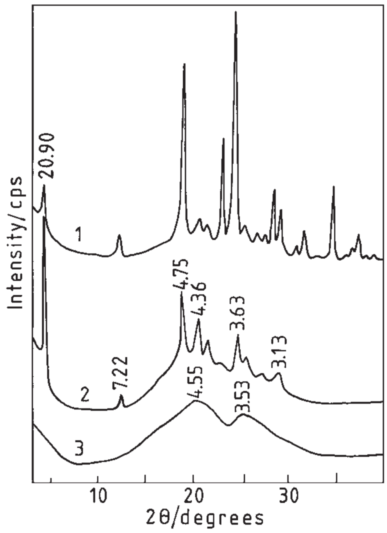
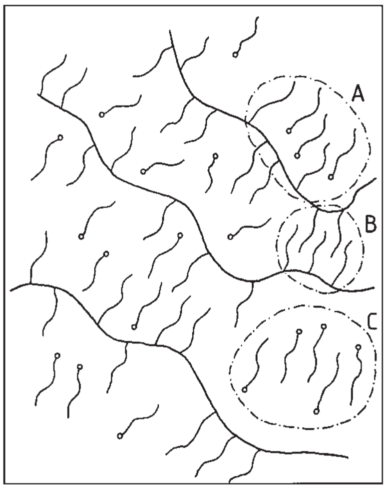


Fig. 2 X-ray diffraction patterns of 1 – PANI–DBSA; 2 – PANI–DBSA partially washed with water; 3 – PANI–DBSA completely washed with water



Scheme 1 Scheme of various types of crystalline regions in the PANI-DBSA system: A – free (non-bonded) DBSA molecules ordered between fixed alkyl tails electrostatically bonded to PANI chains; B – fixed adjacent DBSA alkyl tails electrostactically bonded to PANI chains; C – ordered free (non-bonded) DBSA molecules

PANI–DBSA exhibits a similar well-organized layered structure, in which stacks of charged polyaniline backbones are spaced by the alkyl tails of the DBSA dopant. Thus, we can assume that the large number of crystalline phases are due to the crystallization of the long DBSA alkyl chains in the presence of PANI in the non-uniform spacings obtained between the polymer main chains. On the other hand, we can speculate that DBSA, acting as a plasticizer, induces crystallines order in the rigid-rod matrix of PANI, this order being retained after dedoping of the PANI–DBSA complex.

This is confirmed by the fact that, during the removal of the counterion during washing of the PANI–DBSA with water, the degree of crystallinity gradually falls to ca. 20% and another broad peak appears at 2θ=26° in the X-ray diffraction pattern (Fig. 2, traces 1–3). The washing to constant mass also results in PANI in base form. We assume that, during the preparation of PANI–DBSA, complex crystals built of rigid main PANI chains packed into plate-like layers are formed, with ionic bonded DBSA molecules between them. Crystalline is also formed of the ordered electrostatically fixed adjacent alkyl tails of DBSA (Scheme 1, region B) and of free DBSA molecules which enter the crystalline defects and arrange between the fixed tails acting as nucleation sites (Scheme 1, region A). We consider that the latter are less perfect and are more easily damaged and removed from the polymer system. It can be seen that the reflection peaks at 2θ=30–40° gradually disappear during the washing (Fig. 2, trace 2). Thus, we can assign these peaks to the DBSA paraffinic crystallites. The crystals in which PANI chains are included are more stable, and the crystalline reflection at 2θ=26° is retained after DBSA removal. We recently observed, however, that the polymer obtained after the washing of PANI–HCl under the same conditions is completely amorphous [20]. Hence, it can be stated that the significance of the doping of PANI by DBSA lies in the interaction of the alkyl chains of the acid and the main polymer chains, which leads to structural changes due to a combination of order and mobility in the polymeric system.

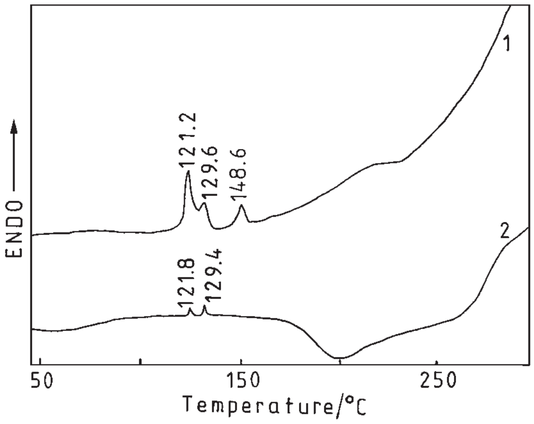


Fig. 3 DSC curves of powdered dry samples of 1 – PANI–DSBA; 2 – PANI–DBSA–EB

The DSC studies of DBSA, PANI–DBSA and PANI–DBSA–EB revealed that, upon heating to 170°C in the calorimetric chamber, the mass losses (determined according to the corresponding equation in the Experimental) were 100, 4 and 8%, respectively. Our previous investigations [21] demonstrated that, in the above-mentioned temperature range (AT-170°C), PANI liberates only absorbed water. It is seen that PANI–DBSA absorbs less water than the EB obtained from it.

The DSC curve of PANI–DBSA, registered after removal of the absorbed water (Fig. 3, trace 1) displays several melting peaks. We assume that these are related to the melting of the crystalline phases formed during the preparation of the PANI–DBSA complex, as mentioned above (Scheme 1). Thus, the DSC investigations confirm our assumption based on the WAXS data that several crystalline phases with different melting temperatures and crystalline structures exist. It may be observed (Fig. 3, trace 2), that after dedoping by the treatment of PANI–DBSA with sodium hydroxide, melting peaks are again registered. We assume that one of these is related to the melting of crystals, including the remaining DBSA macromolecules, while the other reflects the melting of ordered PANI chains. Consequently, it can be stated that DBSA, acting as a plasticizer, induces local order of the PANI rigid-rod main chains, which is retained after removal of the counteranion. Although the peaks of PANI–DBSA–EB are much smaller than those of PANI–DBSA, the presence of crystalline phases is evident. We consider that the registration of the PANI melting peak is a merit of our work since, to the best of our knowledge, this has not been reported to date by other authors.

When PANI–DBSA is heated over 170°C, the mass loss determined up to 350°C is 31.6%, this is due to the liberation of DBSA present as a counteranion (ca. 21.9%), PANI oligomers and decomposition products [21].

On the other hand, heating over 150°C obviously provokes cross-linking of the polymers studied (Fig. 3), as observed previously to proceed in PANI–HCl–EB [21]. The cross-linking at high temperatures, however, damages the layered PANI structure [9]. This is why the crystalline phases disappear during the second heating of the samples in the calorimetric chamber.

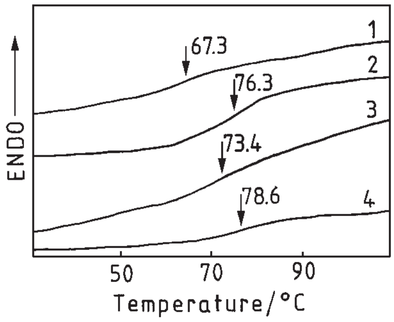


Fig. 4 DSC curves of 1 – powdered dry PANI–DBSA; and 2 – PANI–DBSA; 3 – PANI–HCl–EB and; 4 – PANI–HCl after heating up to 300°C and subsequent quenching

In our earlier DSC investigations of PANI–HCl–EB [21] and PANI–HCl [20], relaxation transitions were observed only for samples preliminarily cross-linked by heating up to 350°C, their temperatures being very close (about 77°C) (Fig. 4, traces 3 and 4, respectively). For PANI–DBSA prepared under the same conditions, however, for the first time we have detected a glass transition temperature both before (T_g=67°C; Fig. 4, trace 1) and after (T_g=76°C; Fig. 4, trace 2) cross-linking of the polymer. We assume that this is due to the increased flexibility of the PANI backbone as a result of the long alkyl tails of DBSA functioning as spacers between the main chains.

Conclusions

The structure of powdered PANI prepared in aqueous medium by the oxidative polymerization of aniline in the presence of DBSA was investigated for the first time. It was found that DBSA induces flexibility and crystallinity in the rigid matrix of PANI, and crystalline phases were observed in PANI–EB after the deprotonation of PANI–DBSA. By means of DSC, a PANI melting peak and a relaxation transition of non-cross-linked PANI were registered, also for the first time.

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