On the Structure of Sulfonic Acid Doped Thermoreversible Polyaniline Gels

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Summary: Thermoreversible polyaniline (PANI) gels of varying weight fraction of PANI are prepared with dinonylnaphthalenesulfonic acid (DNNSA), dinonylnapthalenedisulfonic acid (DNNDSA), (±)-camphor-10-sulfonic acid (CSA) and n-dodecyloxo sulfonic acid (DOSA). The surface morphology is studied using atomic force microscopy (AFM) for 15% PANI concentration (w/w). The AFM study clearly reveals the formation of lamellar morphology in the gel. X–ray scattering experiments of these gels also put evidence for the lamellar structure formation. The lamellar thickness measured from X-ray results remain invariant with composition for PANI-DNNSA and PANI-DNNDSA systems but for PANI-CSA and PANI-DOSA lamellar thickness varies with PANI concentration. Both X-ray diffraction and electron diffraction experiments on the gels of different compositions reveal the existence of new spacings of lower d_{hkl} values which are invariant with composition. These results characterize the formation of new unit cells in the lamella due to the microcrystallization of elongated surfactant tails formed under the doped condition. The d_{hkl} values characterizing the lamellar thickness, bilayer thickness and monolayer thickness are discussed from the molecular models using the MMX program. The variation of lamellar thickness with PANI concentration is discussed from the cohesive force of the surfactant tails within the lamella.

Keywords: atomic force microscopy (AFM); conducting polymers; crystallization; lamellar structure; surfactants

Introduction

Polyaniline (PANI) is an important conducting polymer but is difficult to process because of its highly aromatic nature, interchain hydrogen bonding and charge delocalization.[1,2] Recently, long chain sulfonic acids and phosphonic acids are used both as doping agent and also as processing aids[3-7] for this important polymer. Thermoreversible PANI gels[6,8,9] are produced when the doping process are carried out with larger concentration (> 50%) of long chain sulfonic acid using the swelled PANI lattice in the formic acid medium. Material scientists are

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extremely interested about conducting polymer gels because of the excellent combination of its elastic property and significant electrical conductivity.[10] The conductivity of PANI-sulfonic acid gels has been found to vary on both the doping level and the crosslinking density.[9] The PANI-sulfonic acid systems fulfill all the characteristics (three-dimensional network, reversible first order phase transition)[8,9] of the thermoreversible gel formation.[11]

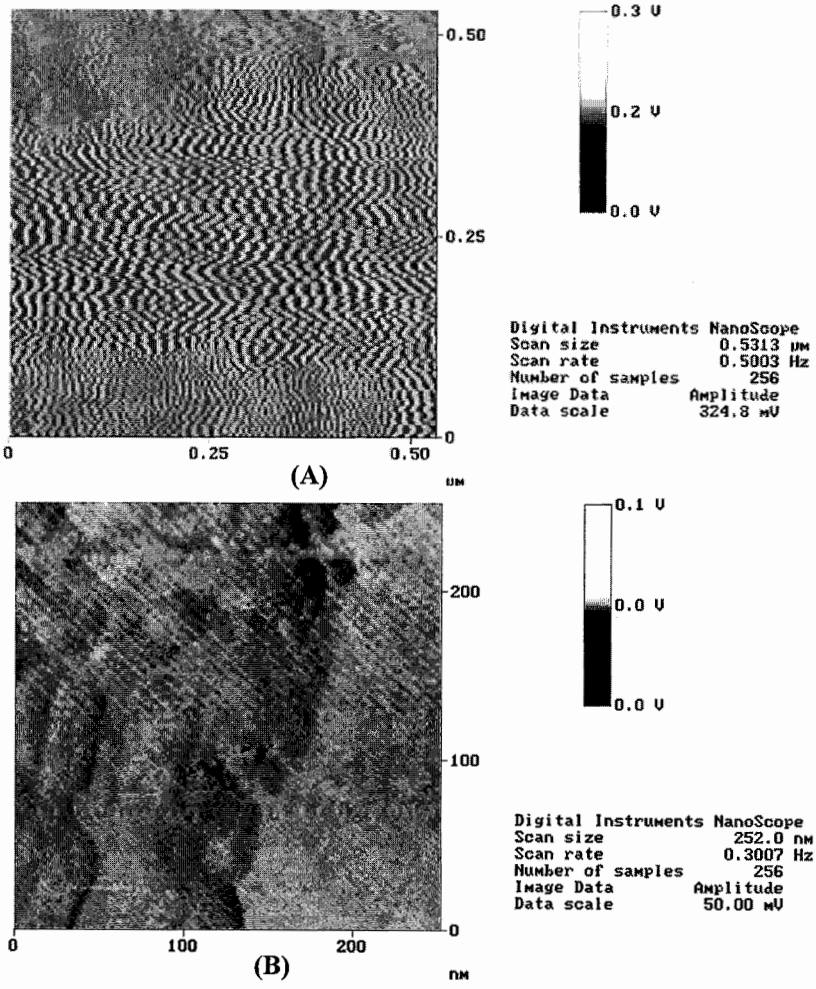
The structure of these gels are not yet clear and is important to elucidate for designing and fabricating of new materials. There is a lot of ambiguity in the mechanism of gelation in this type of polymers. In the PANI-dinonylnaphthalene sulfonic acid (DNNSA), PANI-dinonylnapthalenedisulfonic acid (DNNDSA), PANI-Camphor-10-sulfonic acid (CSA) and PANI-dodecyloxo sulfonic acid (DOSA) gels it has been proposed from thermodynamic study that gelation may occur due to crystallization of the dopants anchored from the PANI chains.[9] The resulting system may, therefore, produce lamellar structure due to both monolayer and bilayer microcrystallization of the doped surfactant molecules to form the lamella. Here, we put some direct experimental evidences towards the formation of lamellar structure of PANI-sulfonic acid gel. The structure of these gels are studied from atomic force microscopy (AFM), wide angle X-ray scattering (WAXS) and electron diffraction experiments. All these results indicate the presence of lamellar structure in the gel. Molecular modeling (MMX program) is used to understand the molecular cause of lamella formation.

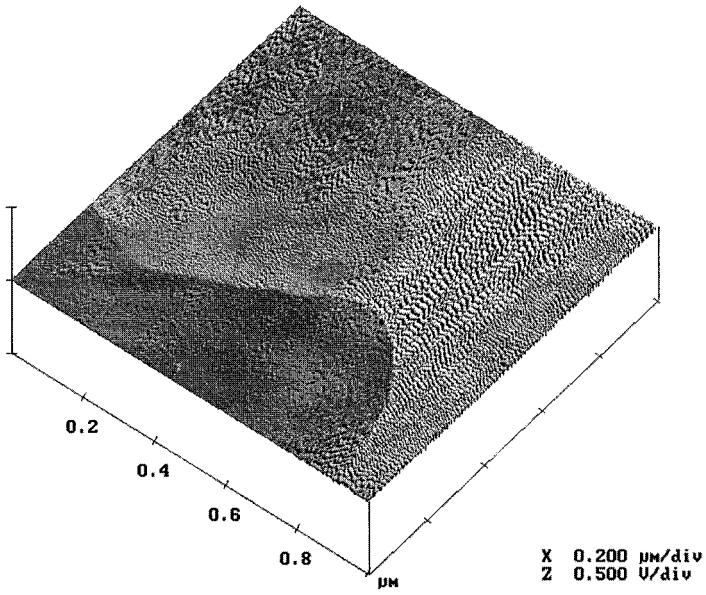
Experimental

PANI was synthesized in the laboratory using standard procedure. The dopants DNNSA and DNNDSA was gift from Dr. P. J. Kinlen, Monsanto Co., St. Louis, USA.[4] CSA was purchased from Fluka and DOSA was prepared using the method described earlier[8,9] The PANI-sulfonic acid gels were prepared from formic acid medium using the procedure described earlier.[8,9] Atomic force microscopy study were done using a D-3000 Nanoscope (Digital Instruments, Santa Barbara, CA) AFM instruments in the tapping mode. The electron diffraction studies of the gel samples were done using a TEM apparatus (Philips CM200). The X-ray diffraction experiment was done using a Rigaku DMAX 2500 diffractometer operating at 40 kV and 150 mA. The samples were scanned in continuous mode with a scan speed 2°/min. The molecular modelings of these gels were performed using a molecular mechanics (MMX) program.[12]

Results

The AFM pictures of the PANI-DNNSA, PANI-CSA gels (W_{PANI} = 0.15) are shown in Figure 1. It is apparent from the figure that the morphology of these gels contains bright strips which are absent in pure PANI.[13] The bright strips may be attributed to the lamella of PANI-surfactant system similar to that of lamellar morphology observed in block-copolymers.[13] Though there are many literature reports on morphology obtained from AFM of acid doped PANI but here we first report the lamellar morphology of the PANI-sulfonic acid system.[13]





(C)

Fig. 1. AFM pictures of PANI-sulfonic acid gels taken in amplitude mode for (A) PANI-DNNSA, (B) PANI-CSA, and (C) PANI-DNNSA (three dimensional).

In Figure 2 the X-ray diffraction patterns of PANI-DNNSA system together with that of PANI (EB) is shown from 2θ value of 2°. It is apparent from the figure that there are peaks in the smaller diffraction angles ($2\theta < 5^{\circ}$) for all the compositions, however, in the higher diffraction angle region ($2\theta > 5^{\circ}$) the crystalline peaks are not prominent except for the diffractrogram for W_{PANI} = 0.40, however, a careful observation on the diffractrograms (W_{PANI} = 0.15 to 0.25) indicate the presence of very small peaks. A comparison of diffractrogram for W_{PANI} =0.40 with that of PANI (EB) (W_{PANI} = 1.0) reveals that the peaks are different from that of PANI (EB). This indicates that some new crystallites are formed from the elongated surfactant tails in this gel and at this composition their concentration is high relative to the composition W_{PANI} = 0.05-0.25. A comparison of AFM picture and lower angle X-ray diffraction data clearly reveals that the d-value of ~30 Å correspond to the lamellar thickness of the gel samples

of this system. The lamellar structure is present for all the compositions (i. e. W_{PANI} = 0.05-0.60) studied here and invariant with composition.

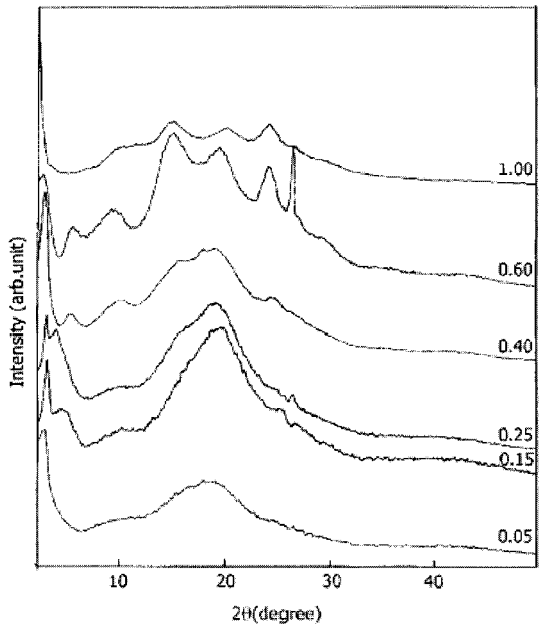


Fig. 2. X-ray diffraction patterns of PANI-DNNSA gels for the indicated weight fraction of PANI.

The X-ray data of PANI-DNNDSA systems also behave similarly like PANI-DNNSA system. But the X-ray results for PANI-DOSA and PANI-CSA systems behaves differently and their lamellar thickness vary with PANI concentration. Besides the lamellar thickness, the bilayer thickness, monolayer thickness of surfactant tails are also obtained from X-ray results. Again the spacings of the crystallites formed from the elongated surfactant tails are also obtained from X-ray results though there are some peaks of pure PANI (EB) particularly at higher PANI concentration.

In order to confirm that there are crystalline entities in the PANI-DNNSA gels (as X-ray diffraction intensities are very poor) the electron diffraction pattern are performed for different gel compositions. The representative electron diffraction pattern for the composition

$W_{PANI} = 0.25$ is presented in Figure 3. The diffraction pattern shows the concentric rings indicating the presence of polycrystalline entities in the sample.

Fig. 3. Electron diffraction pattern for PANI-DNNSA gel (camera length = 1 m) for $W_{PANI} = 0.25$.

The d_{hkl} values calculated from electron diffraction pattern are almost invariant with composition which indicates that the crystallites of surfactant tails formed are of same nature for all the compositions studied here.

It is apparent from the above results that PANI-sulfonic acid gels have lamellar structure and the lamellar thickness values are presented in Table 1. The average lamellar thickness from AFM study (~ 30 Å) tally satisfactorily with the lamellar thickness determined from the X-ray diffraction results. It is important to note that the lamellar thickness (29.4-32.7 Å) is almost independent of gel composition for PANI-DNNSA system. This is probably due to the tight nature of the PANI-DNNSA lamella formed from the crystallization of the surfactant tails of doped DNNSA molecules through the interdigitation of the nonyl tails. A model of the PANI-DNNSA lamella is shown in Figure 4 which is the energy minimized structure using MMX program.[12] The tight nature of the lamella may arise due to the stacking of napthyl groups together with the nonyl tails in the doped condition of DNNSA. Apart from the van der Waal's interaction of dinonyl tails, the interchain attraction through the aromatic napthyl groups are strong enough to produce the tight lamella.

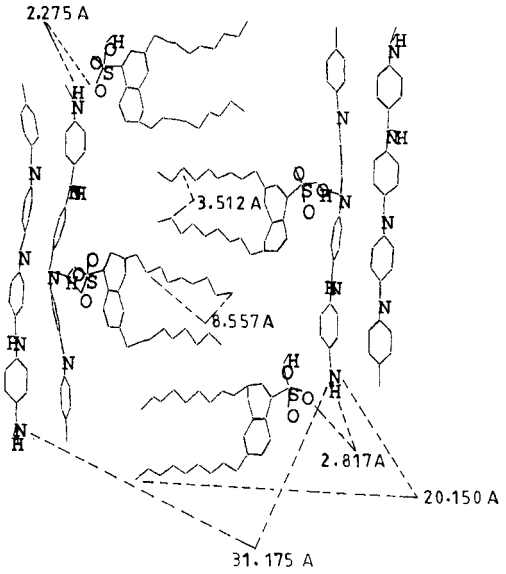


Fig. 4. Molecular modeling of lamellar structure of PANI-DNNSA system after energy minimization through MMX program. The numbers in the figure indicate the distance (Å) between the points in the energy minimized structure.

Table 1. Lamellar thickness (Å) for different PANI-surfactant gel.

gel	Composition (W_{PANI})				
	0.05	0.15	0.25	0.40	0.60
PANI-DNNSA	31.0	29.4	31.0	31.5	32.7
PANI-DNNDSA	26.4	27.0	25.9	26.3	25.2
PANI-CSA	43.0	36.8	27.6	25.9	25.2
PANI-DOSA	34.6	36.0	40.1	42.0	--

In the PANI-DNNDSA system also the lamellar thickness remains invariant with composition similar to PANI-DNNSA system and it can be proved from MMX program. An interesting situation occurs in PANI-CSA system where the lamella thickness decreases with increasing PANI concentration. CSA is a smaller molecule than any of the sulfonic acid used here. Consequently chain interdigitation is not possible with this molecule like the others. A probable explanation for the lamellar structure may be due to the fact that CSA itself is capable of

crystallization with the other CSA molecules forming the lamella (Figure 5). So it dopes the PANI chains and in the middle of the lamella the CSA molecules crystallize under somewhat different condition than in the pure system. With decreasing CSA concentration the interlamellar CSA molecules decrease thereby decreasing the lamellar thickness. This is found to be true for the compositions W_{PANI} = 0.05-0.15-0.25 where a decrease in lamellar thickness by 7-9 Å is observed in each step. This may be clarified from the molecular modeling of PANI-CSA system using MMX program. A CSA molecule has dimension of ~ 9 Å. The lamellar dimension decreases roughly in this order for varying the composition of the gel as W_{PANI} = 0.05-0.15-0.25. So it may be argued from the measured lamellar dimensions that with decreasing CSA concentration from W_{PANI} = 0.05-0.15-0.25 in each step one CSA molecule is lost from the lamella. However, for gel compositions of W_{PANI} = 0.25 to 0.60 the lamellar dimension are almost constant because there may be only two CSA molecules attached side by side to the PANI layers in the lamella and this is the minimum requirement for the lamella formation, fixing the lamella thickness at a fixed value of ~26 Å. In sharp contrast to PANI-CSA system there is an increase in lamella thickness with increasing PANI concentration in the PANI-DOSA gels and at W_{PANI} = 0.60 the lamella is lost. This may be qualitatively explained from the crystallization forces within the lamella. Where the concentration of DOSA is large, all the sites of the PANI chains are fully doped and interdigitation of the surfactant tails is complete. So there occurs a strong cohesive force between the elongated tails of DOSA molecules. This causes a lowest lamellar thickness value for the low value of W_{PANI}. As we increase the PANI concentration, not all the sites are fully doped rather there may be some vacancy. This may lower the crystallization force causing the lamella to expand and it is probably the lamellar situation with increasing the PANI concentration. When the PANI concentration reaches W_{PANI} = 0.60, probably the vacant positions are large enough to loose the crystallization force and the lamella breaks. The difference in lamellar thickness with composition than those of PANI-DNNSA and PANI-DNNDSA systems is probably due to the absence of aromatic ring structure which has stronger cohesive force than the aliphatic chains.

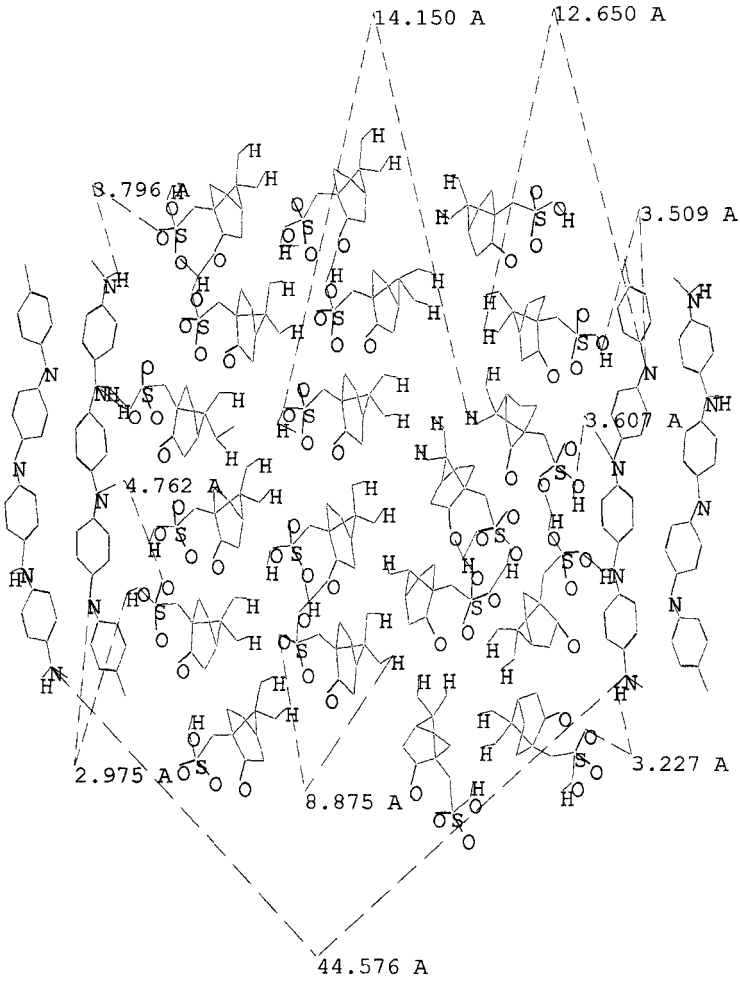


Fig. 5. Molecular model (energy minimized structure) of PANI-CSA system (lamellar thickness = 44.5 A°) using MMX program.

Now when we compare the lower d_{hkl} data with composition, it is observed that d_{hkl} values almost do not changes. These results clearly indicate that the unit cell parameters are constant for the crystallites produced from the surfactant tails. This may offer additional support to the crystallization of the elongated surfactant tails for the lamella development in the PANI-sulfonic acid doped thermoreversible gels.

Conclusion

This study clearly reveals that the structure of PANI-DNNSA doped gels is lamellar and the lamella may be formed due to the interdigitation of elongated surfactant tails under doped condition, followed by their microcrystallization. Atomic force microscopy directly shows the existence of lamella, X-ray studies characterize the lamella and finally the molecular modeling attempts to offer a molecular view for the formation of the lamella. With increasing the PANI concentration in the gels the lamellar thickness and the unit cell parameters of the newly formed surfactant chain crystallites in the lamella remains invariant with composition. This indicates that the unit cells formed from the hydrocarbon tails of the surfactants is almost the same for different compositions of the gel. This study clearly indicates how the surfactant tails of doped sulfonic acid molecule may produce the lamella structure with thermoreversible characteristics.

Acknowledgement

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