Molecular Recognition Solvents for Electrically Conductive Polyaniline

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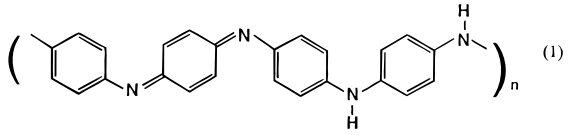
ABSTRACT: Due to its semirigid nature, electrically conductive polyaniline (PANI) has long been regarded as an intractable material, i.e. infusible and poorly soluble in organic compounds. Among the rare exceptions is camphorsulfonic acid (CSA) doped PANI, which exhibits good solubility in *m*-cresol, whereas for other sulfonic acid dopants (e.g. dodecylbenzenesulfonic acid (DBSA)) the solubility in common solvents is poor. We report exceptionally high solubility of fully DBSA and CSA protonated PANI in a crystalline compound, 1,3-dihydroxybenzene, i.e. resorcinol. Up to 20−30 wt % of PANI(DBSA)$_{0.5}$ and PANI(CSA)$_{0.5}$ can be dissolved in resorcinol at 200−220 °C to form particle-free films as observed by optical microscopy. High PANI complex concentrations require high temperatures for dissolution, suggesting UCST behavior with a high critical temperature. Optical microscopy, calorimetry, and X-ray analysis suggest that the solution initially is amorphous. With time, crystallinity develops within the sample, due to partial phase separation of resorcinol while part of it remains miscible. Calculations show that a resorcinol molecule is able to simultaneously form two hydrogen bonds and one phenyl/phenyl interaction with the PANI/sulfonic acid complex, because of their steric match. The conditions required to achieve such matching interactions, i.e. molecular recognition, are discussed. The concept can be extended to find a large category of novel solvents for electrically conductive PANI to yield soluble and fusible complexes.

Introduction

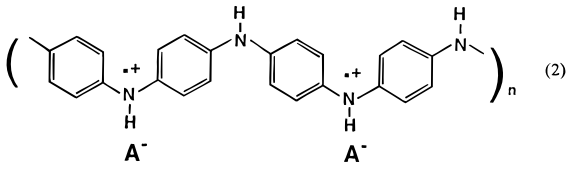
Intrinsically electrically conductive polymers have offered scientists and engineers challenging problems since the invention of H_2SO_4-doped polyaniline in 1971[1] and doped polyacetylene in 1977.[2] One of the main present research areas, of both scientific and industrial importance, has been to develop electrically conductive polymers which are fusible or soluble in common solvents. For electrically conductive polyaniline (PANI), this is not a trivial question because PANI can be regarded as being a semirigid polymer, easily resulting in intractability. Intractability is caused by its highly aromatic nature, the interchain hydrogen bondings, and the charge delocalization effects. Polyaramides can in some respects be considered closely analogous materials.[3]

Polyaniline is one of the most promising conductive polymers due to its straightforward polymerization and excellent chemical stability combined with relatively high levels of conductivity.[4] The so-called emeraldine base (EB) form of PANI is half-oxidized and thus consists of phenylenediamine and quinoid diimine units:



(1)

Emeraldine base is insulating, but its iminic nitrogen sites can be protonated by strong acids to form an acid−base complex.[4] This electrically conductive form is called emeraldine salt. A fully protonated conductive complex is formed when ca. 0.5 mol of protonic acid, A^-H^+, per mol of PhN repeat unit of PANI is used:



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Emeraldine base is soluble only in *N*-methylpyrrolidone (NMP), selected amines, concentrated sulfuric acid, and other strong acids.[5−11] Emeraldine salt is even more intractable. Covalent substitution such as N-alkylation improves melt processability and solubility in various solvents.[12] Melt and solution processability can also be increased if PANI is protonated with a functionalized protonic acid.[13] Specific functionalized dopants[13,14] render high solubility of PANI into particular common solvents,[13] introducing liquid crystallinity in solution[15] as well as in the bulk[16−18] and allowing preparation of solution-cast[19] or melt-processable[14,20] blends with a low percolation limit. Interconnected network structures are obtained in certain solution-cast blends with particular counterions,[19] while in some cases it seems that colloidal dispersions have been obtained.[21−23] The counterions simultaneously act as surfactants for bulk polymers or organic solvents. Well-known examples of such counterions are *p*-dodecylbenzenesulfonic acid (DBSA) and (±)-camphor-10-sulfonic acid (CSA). For example, fusibility and solubility of the fully protonated PANI(DBSA)$_{0.5}$ complex can be obtained by application of additional DBSA.[14,16,24] The effect is probably due to the high strength of hydrogen bonding between the basic PANI moieties and the

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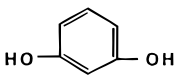
additional strong acid. If the acidity of the additive is reduced, the strength of the hydrogen bonds is reduced, leading to lower solubility.[25] In general, hydrogen bonds between less acidic additives and PANI are not sufficient to render solubilization of the emeraldine salt. For example, aliphatic alcohols, aliphatic carboxylic acids, phthalates and most other carboxylic acid esters, and ketones are not solvents for protonated PANI.[25] Coordination complexes with metal cations and basic amines of PANI have been used to achieve bonding to less acidic plasticizers.[26]

m-Cresol is a low-acidic compound with $pK_a = 10$, yielding particularly interesting properties for PANI protonated by CSA, such as high solubility,[13] lyotropic liquid crystallinity,[15] and extended chain conformations.[27,28] Recently, it has been observed that *m*-cresol is able to induce extended chain conformation also when other counterions are used,[29] albeit the solubility still remains considerably lower than in the case of CSA.[30,31] In a recent study,[31] the system comprising $PANI(CSA)_{0.5}$ and *m*-cresol was studied mainly computationally. It was found that *m*-cresol and other organic solvents with a structure similar to that of *m*-cresol have a possible additional specific interaction with $PANI(CSA)_{0.5}$. The hydroxyl group of the solvent forms a hydrogen bond to the carbonyl group of CSA, and the phenyl rings of PANI and *m*-cresol mutually interact through van der Waals forces leading to stacking of the phenyl rings. This favorable combination of interactions is made possible since the distance between the hydrogen-bonding site in CSA, i.e. the carbonyl group, and the van der Waals bonding site in PANI, i.e. the phenyl ring, match the combined distances of the OH group and phenyl group of *m*-cresol, and the orientating effect of the hydrogen bond makes the phenyl−phenyl interaction feasible. The concept of increased specific interaction between two moieties based on sterical matching is called molecular recognition[32] and it is suggested to promote the solubility of PANI in *m*-cresol. A different form of molecular recognition has also been used to cause helical conformation of PANI.[33,34]

In this work, the dissolution of $PANI(DBSA)_{0.5}$ and $PANI(CSA)_{0.5}$ in crystalline 1,3-dihydroxybenzene, i.e. resorcinol (**3**), is investigated experimentally and computationally. It is observed that both complexes are soluble in resorcinol. As the solubility of $PANI(DBSA)_{0.5}$ in phenols with only one hydroxyl group is small,[25,30] the results indicate that the second hydroxyl group of resorcinol efficiently participates in the specific interaction between resorcinol and $PANI(DBSA)_{0.5}$.[25]



(3)

In order to explain the experimental observations, it has been shown computationally, that a good solvent should be able to form one hydrogen bond and at least two other interactions, i.e. additional hydrogen bonds or phenyl−phenyl interactions, with PANI protonated with generic sulfonic acid.[25] The distances of the hydrogen-bonding moieties of PANI and solvent must match as must the distances of the phenyl rings of the solvent and PANI. According to these results, a novel and more general formalism to enhance specific interactions between electrically conductive PANI and organic compounds using molecular recognition is presented.

Experimental Section

Preparation of the Samples. Polyaniline was polymerized by conventional methods at Neste Oy (Finland) and was further reduced to the EB form with dilute ammonium hydroxide solution.[35]

Two types of protonic acid dopants were used: CSA supplied by Aldrich and DBSA supplied by Tokio Kasei. DBSA was opened and stored in a nitrogen atmosphere to avoid moisture absorption. PANI and CSA were dried under vacuum at 60 °C for 24 h prior to the sample preparation. The protonation was performed according to the procedure by Cao et al.[25] In order to protonate PANI, 0.01 mol of CSA or DBSA was mixed in 50 mL of 99% ethanol until a clear solution was achieved. Subsequently, 0.02 mol of EB (vs PhN repeat unit of EB) was added. The mixture was stirred at 78 °C for 1 h. Ethanol was removed with vacuum distillation at 60 °C, and the complexes were dried under vacuum at 60 °C for 72 h. The resulting materials were stored in a desiccator. The conductivities of the CSA- and DBSA-containing complexes were about 1 S/cm, indicating doping. The formation of the complexes between PANI and the counterions was studied with a Nicolet 60 SX FTIR spectrometer using pressed pellets on KBr crystals. For both complexes, additional evidence of complex formation can be observed as changing of the relative intensities of the characteristic bands in the quinoid region at about 1600 cm^{-1} and in the benzenoid region at about 1500 cm^{-1} [36,37] and widening of the band in the sulfonate region 1150−1000 cm^{-1}. In the following, the resulting complexes are denoted $PANI(DBSA)_{0.5}$ and $PANI(CSA)_{0.5}$, according to the nominal mole fraction of the protonating acid.

Resorcinol (analytical grade, supplied by Fluka) was dried at 60 °C under vacuum overnight. The mixtures of resorcinol with $PANI(DBSA)_{0.5}$ or $PANI(CSA)_{0.5}$ were mixed in a miniature 3 g single-screw mixer at constant elevated temperature in the molten state for 10 min in a N_2 atmosphere and then cooled rapidly (in less than 15 s) to room temperature. The mixing time was limited to avoid thermal degradation, as confirmed later by FTIR. The mixing temperatures were 160, 180, 200, 220, and 240 °C, and the weight fraction of resorcinol was 60, 70, 80, 90, and 100%. The mixtures were dried under vacuum at 60 °C for 24 h and stored in a desiccator.

Optical Microscopy. Optical microscopy in combination with a hot stage was used to study the solubility of electrically conductive PANI in resorcinol at the given concentration and temperature. A small amount of mixture was inserted between two microscope glass slides and kept for 2 min at the temperature where the mixing had taken place, using a Linkam TMS 91 hot stage. The morphology was simultaneously inspected with a Nikon Optiphot 66 microscope. The sample between the glass plates was rapidly cooled, i.e. quenched, to room temperature between two large copper plates. The subsequent development of the morphology at room temperature was inspected as a function of time with an optical microscope.

Most organic compounds such as aliphatic alcohols, ketones, aliphatic esters, and most aromatic esters yield a distinct two-phase structure in which protonated PANI particles are dispersed in a solvent-rich medium.[25] Such distinct two-phase morphologies are typical for poor solvents or nonsolvents. If a homogenously green film without a dispersed phase is observed by optical microscopy, it can be concluded that a higher solubility has been obtained. The latter observation can be made for few materials and conditions, to be described later, and the method is a powerful tool to distinguish between good and poor solvents. However, based on optical microscopy alone, it cannot be specified whether a colloidal dispersion or a true solution is encountered. Therefore, in the following, the optical microscopy results have been denoted as one-phase or two-phase morphologies. Between these two extremes, we found an intermediate region where the PANI particles were swollen by resorcinol.

Infrared Spectroscopy. Infrared spectra of the mixtures containing 10 wt % $PANI(DBSA)_{0.5}$ or $PANI(CSA)_{0.5}$ were measured with a Nicolet 60 SX FTIR spectrometer using

pressed pellets on KBr crystals. A minimum of 64 scans was collected.

Differential Scanning Calorimetry. The DSC measurements were conducted with a Perkin-Elmer DSC 7 instrument. The block temperature was −120 °C, and the calibration was performed using water and indium. The samples were heated to 150 °C at a rate of 10 °C/min and subsequently quenched to −80 °C in order to obtain the best possible signal from a potential glass transition. The second heating run from −80 to +150 °C was measured at a rate of 10 °C/min.

Wide-Angle X-ray Scattering. Wide-angle X-ray scattering experiments were carried out with a Siemens D500 diffractometer in symmetrical reflection geometry using CuKα emission with a curved graphite monochromator mounted in the diffraction beam. The patterns were collected between 2 and 50° 2θ.

Computational Methods

For resorcinol and PANI protonated with CSA, the results are expected to be analogous to our previous results.[31] Therefore, the main emphasis was to model DBSA-protonated PANI in combination with resorcinol. To further simplify the calculations, the long alkyl tails of DBSA, which were not expected to have any essential role in the bonding, were excluded from the model. Therefore, methylbenzenesulfonic acid, i.e. TSA, was selected as the counterion. To investigate the binding of resorcinol molecules to different bonding sites of the PANI/TSA complex, the UHF/AM1 optimized structure of a PANI chain consisting of three rings doped with two TSA molecules was used as a model compound.[31] Four and eight resorcinol molecules, respectively, were then added to the system, and 200 000 steps (time step 1 fs) of molecular dynamics were performed at 300 K. After each 1000 steps, the structure was saved and the resulting 200 structures were optimized. The Insight/Discover software with the pcff force field by Biosym Technologies was used in these calculations.[38,39] As the pcff force field did not have appropriate parameters for the doped PANI chain, the geometry of the chain was fixed into the UHF/AM1 optimized geometry, and the AM1 charges were used.[40] In another computation, water molecules were added to the system to simulate possible tightly bound water, and the subsequent association of resorcinol was studied.

Results

Dissolution Behavior. The solubility of PANI complex in resorcinol depends strongly on the temperature, in addition to the PANI complex weight fraction, as can be observed by optical microscopy (Figures 1 and 2). High temperatures and low PANI complex concentrations promote solubility, and a homogeneous (one-phase) morphology is obtained. The drastic effect of temperature on solubility can be seen in Figure 1 for the mixture containing 30 wt % PANI$(CSA)_{0.5}$. Mixing at 180 °C renders a dispersion of PANI particles, while mixing at 200 °C yields a homogeneous morphology at the resolution of optical microscopy.

Figure 2 depicts the dissolution behavior of the complexes based on optical microscopy. The phase boundary for solubility is shifted toward lower temperatures for CSA-protonated PANI as compared to the DBSA protonation, in good agreement with previously reported results, indicating stronger interaction with CSA than with DBSA.[28,31] At 240 °C, which was the highest mixing temperature, PANI$(DBSA)_{0.5}$ and PANI-$(CSA)_{0.5}$ can be dissolved in exceptionally high concentrations, 30 and 40 wt %, respectively.

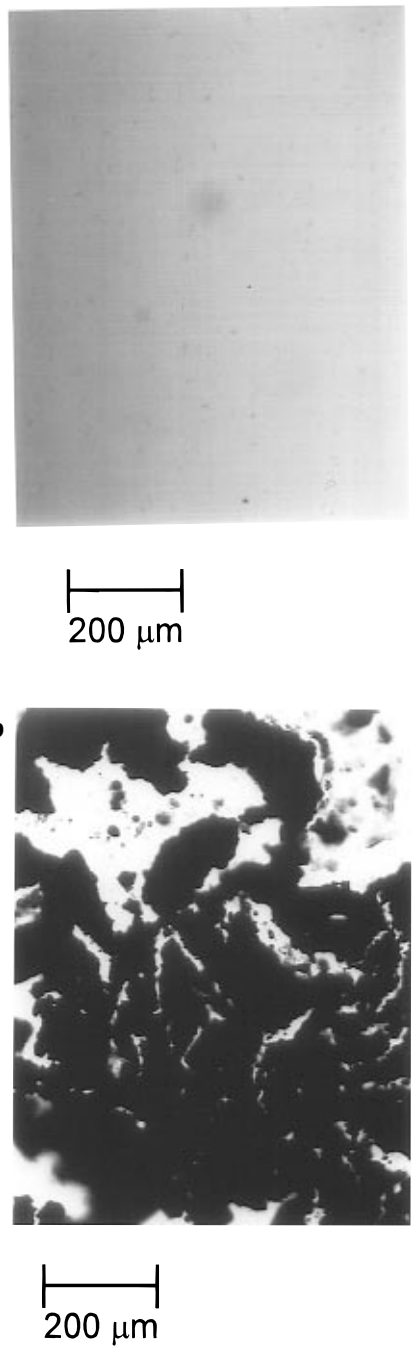


Figure 1. Optical micrographs of the mixture containing 30 wt % PANI$(CSA)_{0.5}$ and 70 wt % resorcinol for the mixing temperatures (a) 200 and (b) 180 °C.

A conventional way to prepare a phase diagram of two solid materials is to mix both components in a common solvent, whereafter the solvent is evaporated. In the present case, there are scarcely common solvents for the PANI complexes and resorcinol, as resorcinol itself is a solvent for PANI complex. The boundary observed in Figure 2 between the one- and two-phase regions is not an accurate prediction for a thermodynamic phase boundary. The type of behavior in Figure 2 corresponds to the right-hand branch of the UCST phase boundary, i.e. the upper critical solution temperature behavior. The critical point is experimentally not achievable due to thermal decomposition at high temperatures.

It could be argued that the shown morphological changes are due to a chemical reaction between PANI complexes and resorcinol and that substantial decom-

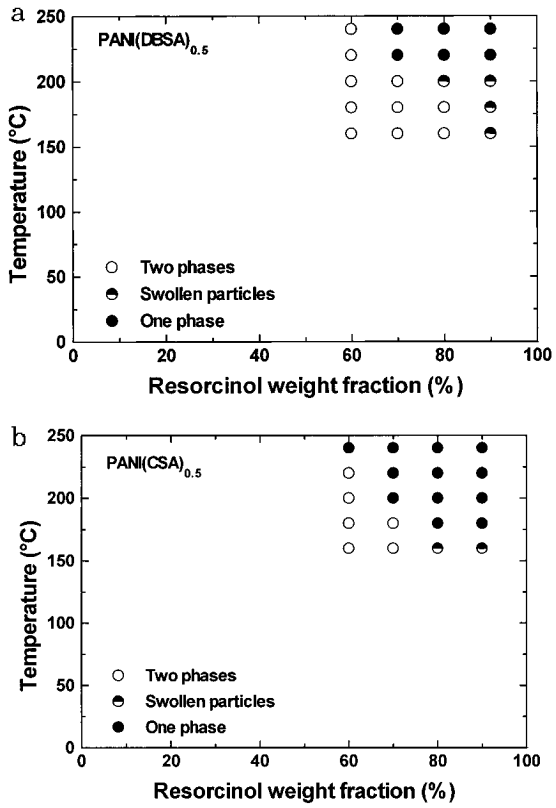


Figure 2. Dissolution phase diagram of (a) PANI(DBSA)$_{0.5}$ and resorcinol mixtures and (b) PANI(CSA)$_{0.5}$ and resorcinol mixtures observed by optical microscopy.

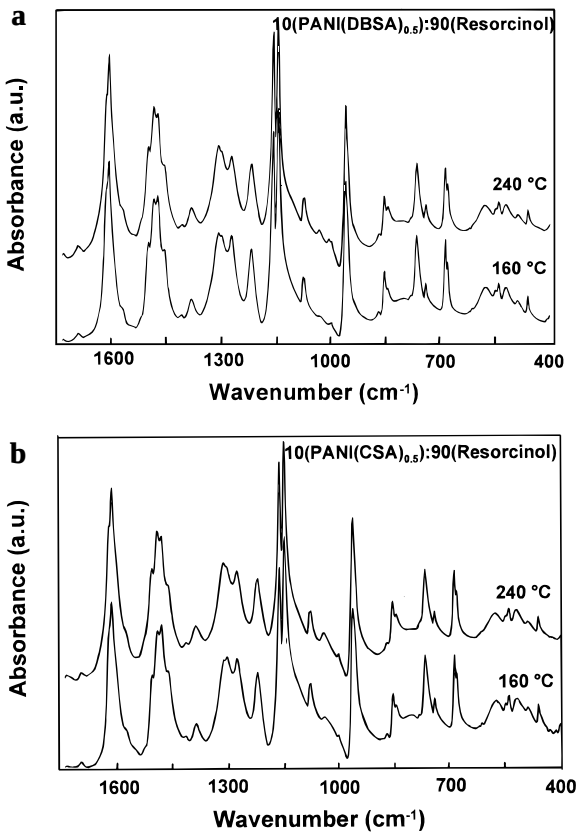


Figure 3. Infrared spectra of the 1700−400 cm^{-1} region for the mixtures containing 10 wt % PANI complex and mixed at 160 or 240 °C: (a) PANI(DBSA)$_{0.5}$ and resorcinol mixtures; (b) PANI(CSA)$_{0.5}$ and resorcinol mixtures.

position would take place at temperatures above 200 °C. To study these arguments, FTIR measurements were carried out on samples containing 10 wt % PANI complex and mixed at different temperatures. The spectra of the mixtures prepared at the lowest and highest mixing temperatures, i.e. 160 and 240 °C, are shown in Figure 3. They show no significant changes as the mixing temperature is increased; i.e. no evidence of major thermal degradation or chemical reactions could be detected by FTIR.

Crystallization Behavior. Resorcinol is a highly crystalline material exhibiting several crystalline modifications.[41] Using optical microscopy, it can be observed that pure resorcinol crystallizes immediately upon quenching to room temperature. In contrast, by polarizing optical microscopy, it is observed that the mixtures of PANI complex and resorcinol show no crystallinity immediately after quenching. Spherulitic types of crystal structures start to grow in an amorphous medium only after a period of time. In addition, the size of the spherulites is smaller for the mixtures. For example, Figure 4 shows spherulitic structure appearing 40 min after quenching the mixture prepared at 200 °C and containing 10 wt % PANI(DBSA)$_{0.5}$. The times for appearance of the first spherulitic crystals were determined using polarizing optical microscopy (Figure 5). The mixing temperature along the *x*-axis affects the time for onset of crystallization. Figure 5 in combination with Figure 2 suggests that higher dissolution increases the time for onset of crystallization. In addition, 20 wt % PANI complex renders longer time for onset of crystallization than does 10 wt % PANI-complex.

In order to study crystallization of the mixtures, WAXS patterns of the quenched sample mixed at 220

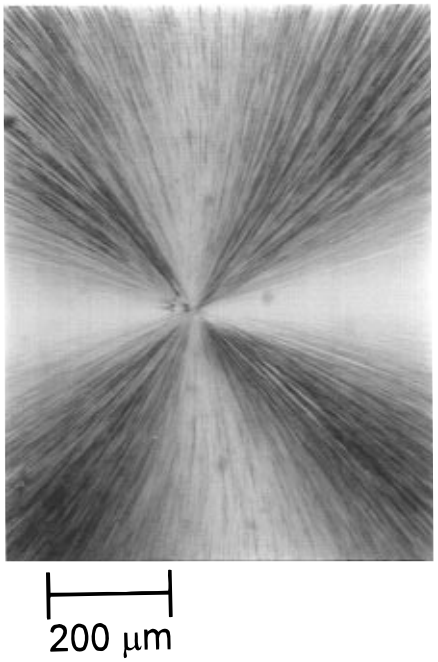


Figure 4. Optical micrograph of one of the spherulitic crystals after aging of the mixture containing 10 wt % PANI(DBSA)$_{0.5}$ and prepared at 220 °C.

°C and containing 30 wt % PANI(CSA)$_{0.5}$ were measured at different aging times at room temperature (Figure 6). An amorphous pattern is obtained after 10 min and still 6 h after the preparation. After 24 h, crystalline reflections are observed, indicating crystallization of resorcinol. The crystal modifications of resorcinol seem to change as a function of aging time.

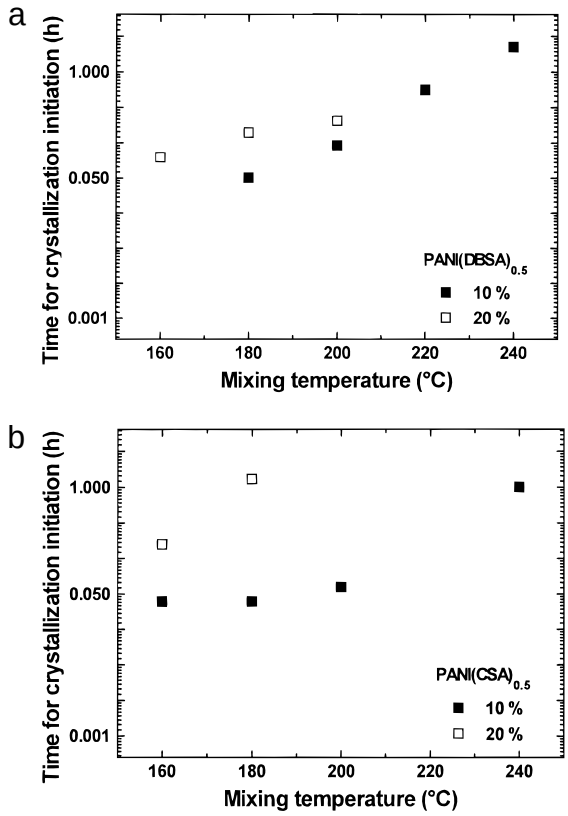


Figure 5. Time for onset of crystallization at room temperature as a function of mixing temperature for the mixtures containing 10 and 20 wt % PANI complex: (a) $PANI(DBSA)_{0.5}$ and resorcinol mixtures; (b) $PANI(CSA)_{0.5}$ and resorcinol mixtures. In the case of the missing points, the time for onset of crystallization is very long, i.e. a few weeks.

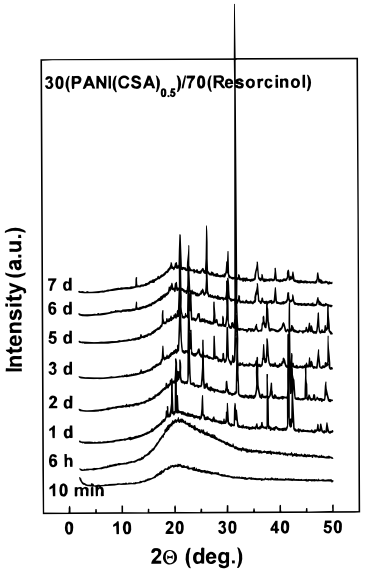


Figure 6. WAXS spectra showing the slow development of crystallinity in a sample consisting of 30 wt % $PANI(CSA)_{0.5}$ mixed at 220 °C.

It can be concluded that mixing resorcinol with PANI complex perturbs crystallization of resorcinol, causing the time for the onset of crystallization to increase from a few seconds to several days or even weeks when the PANI complex is well dissolved in resorcinol and the amount of the PANI complex is increased. The change in crystallization kinetics of resorcinol indicates strong interactions between the components.

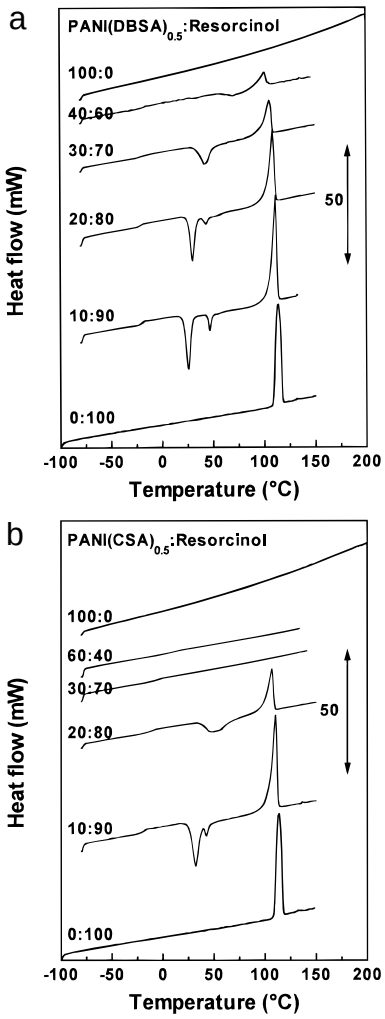


Figure 7. DSC thermograms for the second heating of the pure components and the mixtures prepared at 200 °C: (a) $PANI(DBSA)_{0.5}$ and resorcinol mixtures; (b) $PANI(CSA)_{0.5}$ and resorcinol mixtures.

We suggest tentatively that Figure 2 shows dissolution of the PANI complex in resorcinol, whereas Figures 5 and 6 show the phase separation of the mixtures as a function of time as part of the resorcinol crystallizes, while another part remains miscible with the PANI complex, as will be discussed below in the context of DSC.

Thermal Characterization. The DSC traces of the second heating runs of the samples prepared at 200 °C are shown in Figure 7. The mixtures were aged a few weeks at room temperature. To check that resorcinol had been fully crystallized after this aging time, the DSC traces of some of the samples were measured also 4 months after preparation. The heat of fusion determined from the first heating had not changed during additional aging.

Glass transition, melting, and cold crystallization phenomena can be observed in the thermograms. According to the DSC thermograms, pure resorcinol melts at about 115 °C. The melting temperature decreases as $PANI(DBSA)_{0.5}$ or $PANI(CSA)_{0.5}$ is mixed with resorcinol (Figure 8). For example, as 40 wt % of $PANI(DBSA)_{0.5}$ is mixed with resorcinol at 200 °C, the melting point decreases to about 98 °C. The melting point depression suggests interaction between the components. The mixtures also show cold crystallization of resorcinol during the second heating, which can be

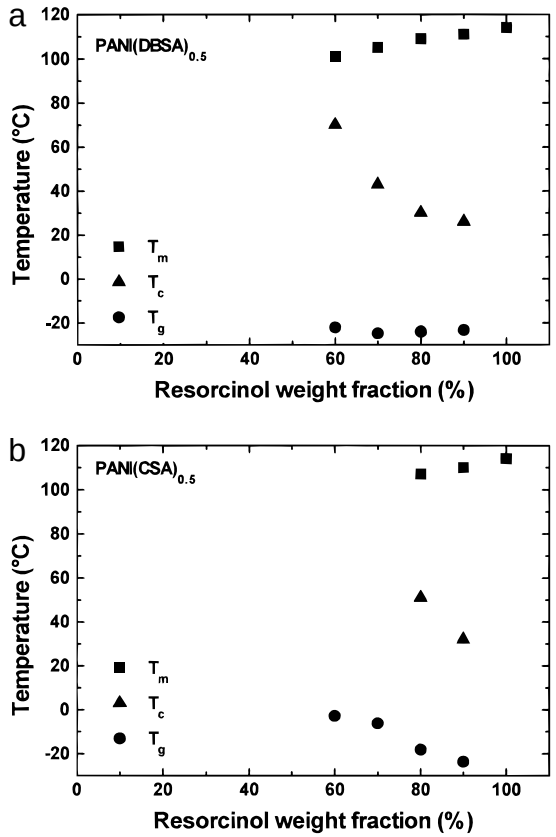


Figure 8. Melting temperatures (T_m), cold crystallization temperatures (T_c), and glass transition temperatures (T_g) of the mixtures and pure resorcinol prepared at 200 °C as a function of resorcinol weight fraction: (a) PANI(DBSA)$_{0.5}$ and resorcinol mixtures; (b) PANI(CSA)$_{0.5}$ and resorcinol mixtures.

related to the crystallization behavior of the quenched samples observed by optical microscopy. Pure resorcinol crystallizes immediately after quenching, and no cold crystallization is observed in the DSC thermogram. The onset of crystallization is perturbed as PANI complex is added, and cold crystallization can be seen for the mixtures. The time for the onset of crystallization is increased as more PANI complex is added, and the temperature of cold crystallization is increased as well (Figure 8). For the mixtures containing 30 and 40 wt % PANI(CSA)$_{0.5}$, the crystallization of resorcinol is suppressed at the time scale of DSC measurement, and no crystallization or melting is observed.

Also the heat of fusion indicates interaction between the components. The heat of fusion determined from the first heating thermogram does not decrease linearly as the weight fraction of resorcinol decreases (Figure 9). This indicates that not all the resorcinol is able to crystallize as part of it interacts strongly with the PANI complex. The interaction seems to be stronger for PANI(CSA)$_{0.5}$ than for PANI(DBSA)$_{0.5}$ since the heat of fusion for the former decreases faster. The heats of fusion determined from the second heating thermograms are somewhat lower, especially in the case of PANI(CSA)$_{0.5}$. This is due to the lower rate of resorcinol crystallization caused by its interaction with the PANI complex.

The glass transition of pure resorcinol cannot be observed due to its high crystallinity at the resolution of the DSC equipment. The glass transitions of the pure PANI complexes are expected to be above 200 °C[24] and cannot be seen in the thermograms. However, for the mixtures glass transitions are observed (Figure 8). The

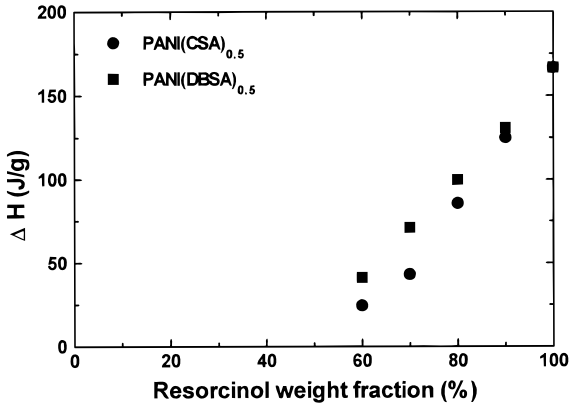


Figure 9. Heats of fusion of the resorcinol melting peak in the first heating as a function of resorcinol weight fraction: (a) PANI(DBSA)$_{0.5}$ and resorcinol mixtures; (b) PANI(CSA)$_{0.5}$ and resorcinol mixtures. The samples have been prepared at 200 °C.

glass transition temperature can be seen to increase as a function of PANI(CSA)$_{0.5}$ weight fraction. The glass transition temperature is about −23 °C for the mixtures containing 10 wt % PANI(CSA)$_{0.5}$ complex and is increased to about −3 °C for the mixtures containing 40 wt % complex. For the mixtures of PANI(DBSA)$_{0.5}$ and resorcinol, the glass transition temperature is about −22 °C and does not depend on the PANI(DBSA)$_{0.5}$ weight fraction. This suggests interaction between resorcinol and the PANI complex is stronger for PANI(CSA)$_{0.5}$ than for PANI(DBSA)$_{0.5}$. The intensity of the glass transition decreases as more PANI complex is added. This implies that the glass transition observed in the thermograms is that of resorcinol.

The melting enthalpy (Figure 9) suggests that on average 2.8 mol of resorcinol vs PANI repeat unit is miscible with either of the complexes, while the rest crystallizes into a pure resorcinol phase.

WAXS Measurements. The results of the WAXS measurements for the mixtures prepared at 200 °C are shown in Figure 10. Phase separation is evident from the patterns as the measurements were conducted at room temperature a few weeks after preparation. Pure resorcinol exhibits several crystalline modifications depending on its thermal history. This could be observed as different combinations of sharp peaks after heat treatment at different temperatures. The diffraction patterns of PANI(DBSA)$_{0.5}$/resorcinol mixtures are very similar. Resorcinol crystallizes in the same manner in all the samples, and the layer peak related to PANI(DBSA)$_{0.5}$ at 25−27 Å is also observable in the patterns. PANI(CSA)$_{0.5}$/resorcinol mixtures show more variations in the crystallization behavior of resorcinol. The same crystal modification as observed in the PANI(DBSA)$_{0.5}$/resorcinol mixtures is dominant at high resorcinol contents (80 and 90 wt %) and/or at low temperatures (160−180 °C). Pure PANI(CSA)$_{0.5}$ does not show any layer peak in contrast to pure PANI(DBSA)$_{0.5}$, but a layered structure is obtained for the mixtures (Figure 10).

The observation that mixing resorcinol with PANI complex favors a certain crystalline modification is an additional indication of strong interactions between the components. Broadening of resorcinol peaks observed for all the mixtures is further evidence of interaction.

Calculations. Sulfonate groups have a strong orientational effect on the resorcinol molecules.[31] In the anhydrous case, bonding of resorcinol to sulfonic acid

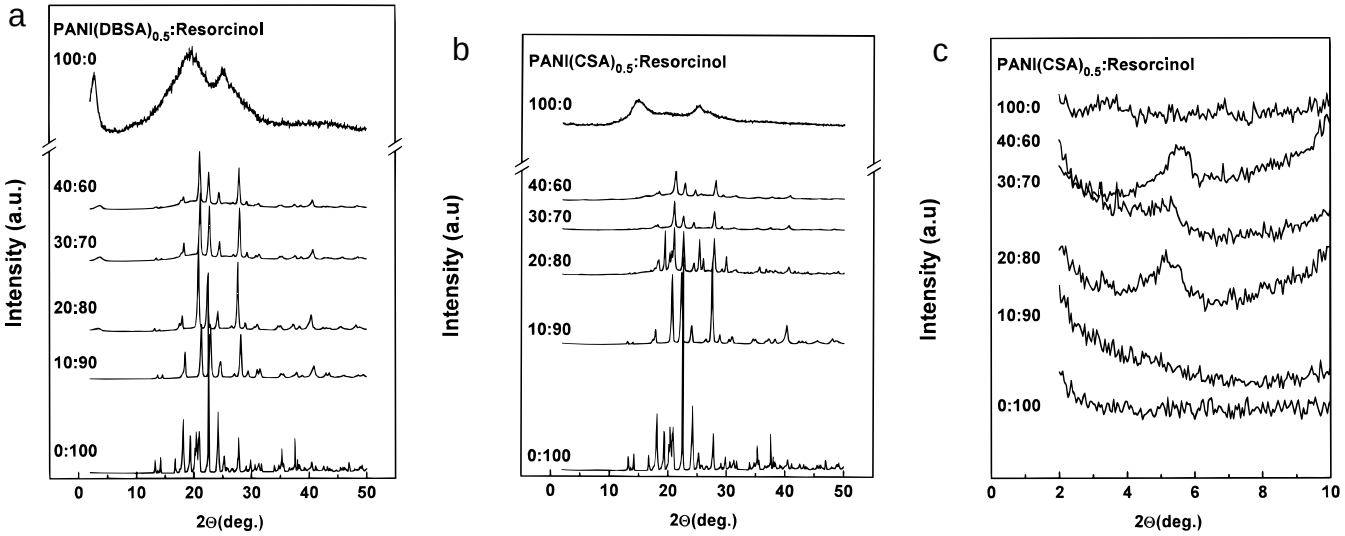


Figure 10. WAXS diffraction patterns for the pure components and the mixtures prepared at 200 °C: (a) PANI(DBSA)$_{0.5}$ and resorcinol mixtures (the diffraction pattern of pure PANI(DBSA)$_{0.5}$ is magnified tenfold with respect to the other patterns); (b) PANI(CSA)$_{0.5}$ and resorcinol mixtures (the diffraction pattern of pure PANI(CSA)$_{0.5}$ is magnified tenfold with respect to the other patterns); (c) magnification of the patterns of PANI(CSA)$_{0.5}$ and resorcinol mixtures showing the layer peak.

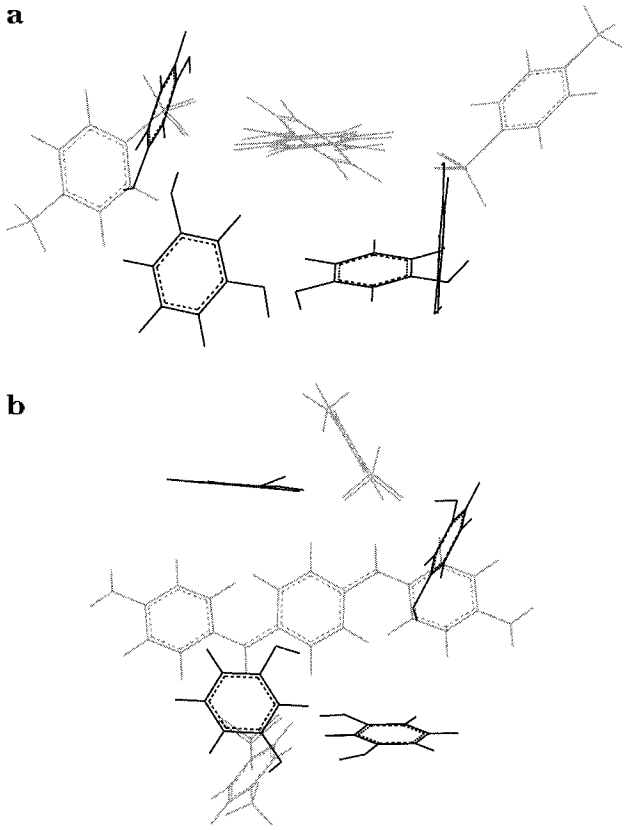


Figure 11. Example of an optimized structure for a PANI/TSA model compound with four resorcinol molecules viewed (a) along the chain and (b) from the top of the chain. The resorcinol molecules are colored dark, and the PANI/TSA complex gray.

doped PANI is studied using a model compound consisting of three PANI repeat units, doped by two TSA molecules. Up to four resorcinol molecules can form strong hydrogen bonds directly to the two sulfonate groups. A typical optimized structure is shown in Figure 11. In this case, the association of resorcinol is dominated by the strong orientational effect of the sulfonate group on one of the hydroxyl groups of resorcinol. Therefore, no stacking of resorcinol on top of PANI phenyl rings due to phenyl/phenyl interaction

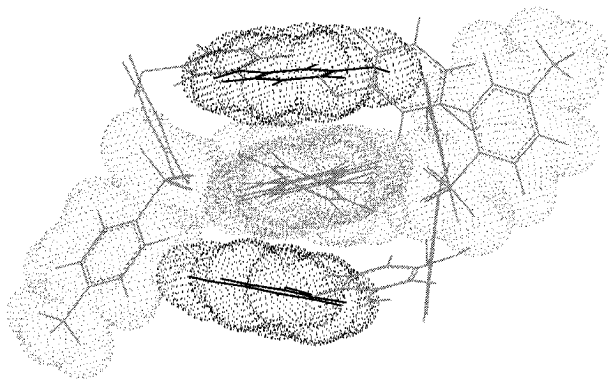


Figure 12. Example of an optimized structure for a PANI/TSA model compound with eight resorcinol molecules viewed along the chain. The PANI/TSA model compound and the resorcinol molecules on the top of the chain are shown with their van der Waals surfaces.

is suggested. As a conclusion, 1−2 mol of resorcinol vs PANI PhN repeat units can be strongly bound to anhydrous sulfonates when PANI is fully protonated by TSA.

The nature of the available interactions changes if the strong polarity of the sulfonate is shielded by additional molecules between the interacting resorcinol and the sulfonate. For example, if more than four resorcinol molecules are brought into contact with the above PANI/TSA model compound, bonding of the additional resorcinol molecules to sulfonates is sterically hindered by the first four resorcinol molecules. The association of eight resorcinol molecules is depicted in Figure 12. The additional resorcinol molecules are bonded both by hydrogen bonds and by phenyl/phenyl interactions on top of the PANI rings. The ring-to-ring distance in the optimized structure is 3.5−5.7 Å. The polarity of the sulfonate group can also be shielded by the presence of bound water, as it is expected that in sulfonic acid protonated PANI there are always some bound water molecules present due to the high polarity of the sulfonate groups. Therefore, a system consisting of the above PANI/TSA model compound, seven water molecules, and one resorcinol molecule was studied (Figure 13). In all the optimized structures, the water molecules occupy the binding sites around the sulfonate groups,

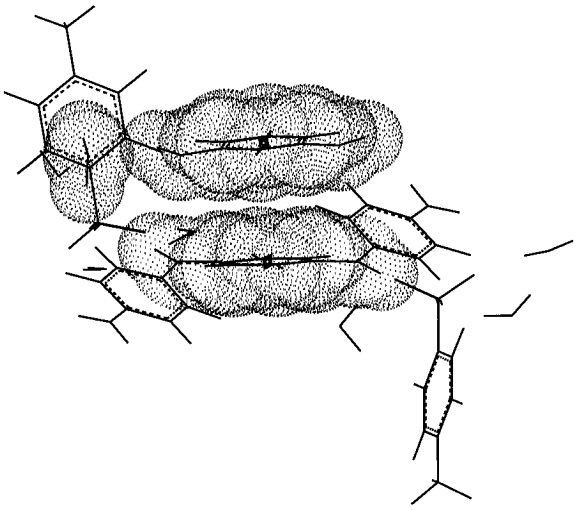


Figure 13. PANI/TSA model compound with seven water molecules and one resorcinol molecule. The chain and the resorcinol molecule are shown with their van der Waals surfaces.

and the resorcinol molecule was on top of the chain due to phenyl/phenyl interaction, the inter-ring distance being 3.7−4.0 Å. The hydroxyl groups form hydrogen bonds with the water molecules bound to the sulfonate groups.

One can conclude that bonding of resorcinol to the PANI complex is a complicated phenomenon, where the local surroundings of the sulfonates determine the available associations. Sulfonate groups are able to orientate the resorcinol molecules due to their strong dipole moment in which case no phenyl/phenyl stacking is observed. However, when this dipole moment is shielded by bound water or by a "first layer" resorcinol, its orientational effect is reduced, allowing phenyl/phenyl stacking of a "second layer" of resorcinol molecules, thus allowing molecular recognition.

Discussion

Electrically conductive polyaniline was long considered to be an intractable material, infusible and insoluble in common organic solvents. A standard approach to address problems concerning insolubility is to use solubility parameters.[42,43] The method is inaccurate even for a flexible nonassociating polymer such as polystyrene,[44] and its use in the context of electrically conductive PANI is expected to be highly unreliable. It is known that because of their strong hydrogen-bonding ability, several strong acids are solvents for electrically conductive PANI. For example, PANI(DBSA)$_{0.5}$ is soluble in additional DBSA[16] or other sulfonic acids. The highly acidic solvents do not allow convenient methods to prepare fusible PANI complexes because of their extreme corrosivity. For compounds of lower acidity, the ability to solubilize the complex is usually lost. For example, mixtures of PANI complex and aliphatic alcohols form two-phase systems.[25] CSA-doped PANI is highly soluble in *m*-cresol (2−10 wt %[14]) and in some other phenols[14,30] while changing the counterion to DBSA yields considerably poorer solubility (1 wt %[30]), and for methanesulfonic acid even less. Albeit *m*-cresol is able to induce extended conformations,[29] it is not an effective solvent for PANI with a generic sulfonic acid counterion. Based on model calculations, we have recently suggested[31] that the uniquely synergistic behavior of CSA counterions in combination with simple phenols, such as *m*-cresol, is due to molecular recognition: the OH group of *m*-cresol is hydrogen bonded to the carbonyl group of CSA, while its phenyl group is on top of an aromatic PANI ring due to phenyl/phenyl interaction. Both interaction energies add, because *m*-cresol can sterically be fitted so that the two interactions are allowed simultaneously. Changing the counterion, for example to DBSA or TSA, does not allow both interactions to occur, and as a result lower solubility is observed.

The aim of this work was to identify novel molecular recognition principles that can be applicable to PANI protonated by generic sulfonic acid. We earlier observed that, compared to simple phenols, substituted phenols having additional hydrogen-bonding moieties or aromatic rings directly attached to its aromatic ring improved solubility.[25] The simplest of such compounds are dihydroxybenzenes and phenylphenols, the natural extension being bisphenols.

In this work, 1,3-dihydroxybenzene (resorcinol) was selected as a model compound to study the solubility properties of PANI(CSA)$_{0.5}$ and PANI(DBSA)$_{0.5}$. The solubility of PANI(CSA)$_{0.5}$ and PANI(DBSA)$_{0.5}$ in resorcinol was studied at elevated temperatures. The solubility of the PANI complex in resorcinol is strongly temperature dependent. Low concentrations of PANI complex and elevated temperatures favor dissolution. The observed dissolution behavior below 240 °C suggests an UCST behavior. Melting point depression shows evidence of strong interaction between the components. WAXS and DSC show that PANI(DBSA)$_{0.5}$ and PANI(CSA)$_{0.5}$ have a strong effect on the crystalline modification of resorcinol. Infrared spectroscopy of PANI complex in resorcinol was made outside this work to study interaction between the components. Differences in resorcinol crystallization mask other changes in the spectra, but evidence of hydrogen bonding and ring interactions could be observed and will be published in detail later.

PANI(DBSA)$_{0.5}$/resorcinol and PANI(CSA)$_{0.5}$/resorcinol mixtures showing an amorphous character immediately after quenching to room temperature became birefringent after aging at room temperature. The observation was confirmed by WAXS measurements. One can conclude, that the PANI complexes effectively perturb the crystallization of resorcinol if the mixing is made in the part of the phase diagram where high dissolution is encountered. By analysis of the crystallization enthalpy of resorcinol, it is shown that part of the resorcinol is miscible with PANI(DBSA)$_{0.5}$ and PANI(CSA)$_{0.5}$, while the remaining part of resorcinol crystallizes; i.e. phase separation takes place.

Computationally, a net interaction is observed where resorcinol interacts with the protonated PANI by using three simultaneous interactions: phenyl/phenyl interaction on top of the PANI aromatic ring and two hydrogen bondings to the sulfonates mediated by the bound water molecules. This type of interaction comprises a novel type of molecular recognition. It is also observed that even in the anhydrous case, the first layer of bound resorcinol molecules can act as further bonding sites for additional resorcinol molecules, in which case the molecular recognition principles also can be fulfilled.

One of the essential conditions for solubility found in context of this and related studies[25,31] is that in sulfonic acid doped PANI there is a repeating pattern: six-membered aromatic rings at distances of ca. 6 Å capable of phenyl/phenyl interactions, and exactly at the same

periodicity there are either aminic moieties or protonated iminic moieties in combination with the highly polar sulfonates. For an aromatic additive fulfilling the same periodicities, strong interaction can be anticipated, resulting in fusibility or solubility. The additional requirements are that the hydrogen-bonding moieties have to be able to make strong enough hydrogen bonding and the compound has to be rigid enough to maintain its steric dimension against thermal movements.[25] Having realized the underlying principle, it becomes evident that the compounds are not limited to phenols with the OH group hydrogen-bonding units. Any compound fulfilling the same requirements of phenyl/phenyl interaction and hydrogen-bonding periodicity is acceptable. Therefore, instead of using OH groups, one can use COOH or other groups forming strong hydrogen bonds.[25]

Conclusion

The results of this work show that individual small interactions such as hydrogen bonding and phenyl/phenyl interactions can be combined to yield macroscopic interactions to render intractable polymer, i.e. PANI−sulfonic acid complex, highly soluble in additives of low polarity. CSA-protonated PANI with its high solubility in *m*-cresol is the limiting case toward this direction, as we have suggested previously.[31] An additional example, related to the present work, is that 10 wt % PANI protonated by TSA, DBSA, or CSA is soluble in 90 wt % resorcinol when the mixing is performed at elevated temperatures, i.e. ca. 200−220 °C. Solubilization requires several sterically matched interactions with the amine−amine, protonated imine−amine, and the 6 Å ring−ring periodicities of the PANI complex. The combination of complexes and chemical compounds capable of what is called molecular recognition requires careful molecular-level architecture and can be used to construct polymer structures at the molecular level in analogy with DNA.

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