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INVESTIGATIONS OF FUNCTIONAL ELECTROACTIVE POLYMERS

Doctoral Dissertation

Mari Tiitu



**Helsinki University of Technology
Department of Engineering Physics and Mathematics
Optics and Molecular Materials**

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Department of Engineering Physics and Mathematics
Optics and Molecular Materials**

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Abstract Conjugated polymers containing pi-conjugated backbones form a scientifically and technologically important class of polymers. In their undoped form they are semiconductors, but they can be doped for electrical conductivity, and allow redox-activity, which all can lead to functional materials. One of the most important conjugated polymers in large scale applications is polyaniline due to its economics and good stability. Polyaniline is used for applications requiring conductivity as well as corrosion inhibition. In this thesis, conducting network structures based on acid doped polyaniline are prepared within solvent and polymer matrices, in order to investigate percolation phenomena. Self-assembled structures have been investigated to study confinement of the polyaniline chain in nanosized domains and its effects on conductivity. A concept was identified and patented to achieve a novel anticorrosion coating based on polyaniline/epoxy compositions. In some applications ionic or protonic conductivity is preferred instead of electronic conductivity. These include e.g. fuel cell membranes or applications where colorless conductive materials are needed. The thesis describes a model material for fuel cell membranes, where the mechanical and conductivity properties can be separately tailored due to self-assembly, as well as a novel material to allow colorless antistatic paper coatings. This thesis consists of an overview and of the following 6 publications: 1. O. Ikkala, M. Tiitu, J. Tanner, J. Ruokolainen, Synth. Met., 102, 1248-1249, (1999). 2. M. Tiitu, P. Hiekkataipale, J. Hartikainen, T. Mäkelä, O. Ikkala, Macromolecules, 35 (13), 5212-5217, (2002). 3. M. Tiitu, N. Volk, M. Torkkeli, R. Serimaa, G. ten Brinke, O. Ikkala, Macromolecules, 37 (19), 7364-7370, (2004). 4. M. Tiitu, M. Torkkeli, R. Serimaa, T. Mäkelä, O.T. Ikkala, Solid State Ionics 176, 1291-1299 (2005). 5. M. Tiitu, A. Talo, O. Forsén, O. Ikkala, Polymer 46, 6855-6861 (2005). 6. M. Tiitu, J. Laine, R. Serimaa, O. Ikkala, Journal of Colloid and Interface Science, accepted (2006).			
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Preface

This work has been carried out in the Centre of Excellence of Academy of Finland ("Bio- and Nanopolymer Research group", 77317) at the Department of Engineering Physics and Mathematics at Helsinki University of Technology under supervision of academy professor Olli Ikkala. I would like to thank him for the encouragement as well as the enthusiasm and new ideas he has been able to diffuse.

I wish to thank important collaborators professor Ritva Serimaa and Ph.D. Mika Torkkeli for help and discussions and their expertise in x-ray scattering. I would like to express my thanks to Lic.Sc. Tapio Mäkelä for numerous discussions and helpful instruction. Professor Matti Kaivola, professor Heikki Tenhu, academy research fellow Janne Ruokolainen, professor Olof Forsén and professor Janne Laine deserve my thanks as well. I also want to thank the pre-examiners Dr. Charl Faul and professor Ronald Österbacka for revision suggestions that helped to improve the manuscript.

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Finally, I wish to thank my friends and relatives for all the care and support.

List of used abbreviations and symbols

AMPSA	2-acryloamido-2-methyl-1-propanesulfonic acid
CMC	carboxymethyl cellulose
C _n res	4-alkylresorcinol, tail length n
C _n TAC	alkyltrimethylammonium chloride, tail length n
CSA	camphor sulfonic acid
DBSA	dodecylbenzenesulfonic acid
DETA	diethylenetriamine
DGEBA	diglycidyl ether of bisphenol-A (epoxy resin)
DMAc	<i>N,N</i> -dimethylacetamide
DMF	dimethyl formamide
DMPU	<i>N,N'</i> -dimethylpropyleneurea = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1 <i>H</i>)-pyrimidone
EB	emeraldine base
ES	emeraldine salt
HFIP	hexafluoro-2-propanol
HMPA	hexamethylphosphoramide
HOMO	highest occupied molecular orbital
IPDA	isophorone diamine
LEB	leucoemeraldine base
LUMO	lowest unoccupied molecular orbital
NMP	<i>N</i> -methyl-2-pyrrolidone
P4VP	poly(4-vinylpyridine)
PANI	polyaniline
PNB	pernigraniline base
PS	polystyrene
SAXS	small angle X-ray scattering
SEBS	polystyrene- <i>block</i> -poly(ethylene/butylene)- <i>block</i> -polystyrene
THF	tetrahydrofuran
TMDA	trimethylhexanediamine
TMU	tetramethylurea
UV-Vis-NIR	ultraviolet/ visible/ near-infrared spectroscopy
WAXS	wide angle X-ray scattering
a_h	horizontal shift factor
a_v	vertical shift factor
E_a	activation energy
E_{OCP}	open circuit potential
f	frequency
G'	storage modulus
G''	loss modulus
G_0	static elastic modulus
$G(t)$	shear relaxation modulus
I	scattering intensity
J_e^0	steady state creep compliance

k	Boltzmann constant
L	length (in Paper I)
L	long period of self-assembled structure
L_0	initial length
p	reaction coordinate
p_c	critical reaction coordinate
q	magnitude of scattering vector
R_p	polarization resistance
s	critical exponent s
t	critical exponent t
T	temperature
t_g	gel time
x	molar fraction
y	molar fraction
W	activation energy
γ	strain
Δ	critical exponent Δ
δ	phase angle
ε	distance from the critical point
λ	wavelength
λ	relative elongation (in Paper I)
η_0	static viscosity
σ	electrical conductivity
τ	relaxation time
τ_z	longest relaxation time
ω	frequency ($2\pi f$)

Papers

Paper I: O. Ikkala, M. Tiitu, J. Tanner, J. Ruokolainen, *Blends of Thermoreversible Gels of Polyaniline with Thermoplastic Elastomers: Co-continuous Melt Processible Polymer Structures*, **Synth. Met.**, **102**, 1248-1249, (1999).

Paper II: M. Tiitu, P. Hiekkataipale, J. Hartikainen, T. Mäkelä, O. Ikkala, *Viscoelastic and Electrical Transitions in Gelation of Electrically Conducting Polyaniline*, **Macromolecules**, **35** (13), 5212-5217, (2002).

Paper III: M. Tiitu, N. Volk, M. Torkkeli, R. Serimaa, G. ten Brinke, O. Ikkala, *Cylindrical Self-Assembly and Flow Alignment of Comb-Shaped Supramolecules of Electrically Conducting Polyaniline*, **Macromolecules**, **37** (19), 7364-7370, (2004).

Paper IV: M. Tiitu, M. Torkkeli, R. Serimaa, T. Mäkelä, O.T. Ikkala, *Self-Assembly and Flow Alignment of Protonically Conducting Complexes of Polystyrene-block-Poly(4-vinylpyridine) Diblock Copolymer with Phosphoric Acid*, **Solid State Ionics** **176**, 1291-1299 (2005).

Paper V: M. Tiitu, A. Tallo, O. Forsén, O. Ikkala, *Aminic Epoxy Resin Hardeners as Reactive Solvents for Conjugated Polymers: Polyaniline Base/Epoxy Composites for Anticorrosion Coatings*, **Polymer** **46**, 6855-6861 (2005).

Paper VI: M. Tiitu, J. Laine, R. Serimaa, O. Ikkala, *Ionically Self-Assembled Carboxymethylcellulose-Surfactant Complexes for Antistatic Paper Coatings*, **Journal of Colloid and Interface Science**, accepted (2006).

Author's contribution

Paper I: The author has contributed in sample preparation, measurements, analysis and drawing of the figures, and taking part in planning the experiments and writing the manuscript.

Paper II: The author has participated in the planning of the experiments, prepared all the samples, performed most of the measurements and analysis, constructed the viscoelastic master curves, drawn the figures, and prepared the first version of the manuscript.

Paper III: The author has taken part in the design of the experiment, done all of the sample preparation, conductivity measurements, conductivity analysis and large-amplitude oscillatory shear flow, and written the first version of the manuscript. She also has measured the small-angle X-ray data and participated in the analysis.

Paper IV: The author has taken part in the design of the experiment and done a part of solubility testing. She has carried out the sample preparation, conductivity measurements, conductivity analysis and large-amplitude oscillatory shear flow, and written the first version of the manuscript. She has also measured the small-angle X-ray data and participated in the analysis.

Paper V: The author has taken part in the sample preparation and solubility testing. She also has participated in the designing the coating concepts, planning and carrying out the immersion test, and has done the analysis of the immersion test.

Paper VI: The author has taken part in the design of the experiment, done all of the sample preparation and most of the conductivity measurements. Conductivity analysis has been her responsibility. She also has measured the small-angle X-ray scattering data and participated in the analysis.

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List of used abbreviations and symbols

Papers

Author's contribution

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Introduction

Conjugated polymers containing π -conjugated backbones form a scientifically and technologically important class of polymers. In their undoped form they are semiconductors, but they can be doped for electrical conductivity, and allow redox-activity, which all can lead to functional materials. One of the most important conjugated polymers in large-scale applications is polyaniline due to its economics and good stability. Polyaniline is used eg. for applications requiring conductivity as well as corrosion inhibition [1].

The structures at different length scales, ranging from the molecular scale up to the macroscopic scale, need to be understood and controlled to fully use the application potential of polymeric materials. Molecular self-assembly allows well controlled nanoscale structures due to competing molecular level interactions and allows tailoring of the material properties and even allows hierarchies [2-10]. For example conductivity can be tuned by self-assembled structures, eg. addition of a non-conducting compound to a conducting polymer causes conductivity enhancement, in spite of dilution of the conducting compound [11]. Self-assembly usually leads to only local ordering. Orientation of self-assembled structures using external fields, such as flow [12-19] or electric field [20-25], can be used to achieve anisotropic properties on a macroscopic scale.

Conductivity of polymeric materials can be achieved also by transport of protons and ions. Protonically conducting materials are important for fuel cell membranes, see eg. [26]. For protonically conducting materials, anisotropic conduction and concepts for separate tailoring of the conductivity and the mechanical properties due to self-assembly have been shown [27, 28], as well as smart materials where protonic conductivity can be switched based on the phase transitions within the self-assembled structures [29].

On the other hand, network formation upon gelation manifests itself in the mechanical properties [30, 31]. If a conducting polymer takes part in the network formation, conductivity can also be affected [32]. Percolation of the charge-carrier species is the key to high conductivity and control of the percolation can allow functional materials with responsive conductivity.

This thesis describes some concepts to tailor properties of polymeric materials for a variety of applications using electroactive and conjugated polymers. Papers III and V related to conductivity and corrosion inhibition properties of polyaniline will be addressed first in the text. Ionic conductors and results of papers IV and VI will then be described. Last, papers I and II related to gels and networks of conducting polymers and their effect on conductivity will be described.

Conjugated polymers

The phrase “conjugated polymers” typically refers to polymers with spatially extended π -bonding system. Usually conjugated polymers have an energy gap between the highest occupied molecular orbital (HOMO) level corresponding to the fully occupied π -band and the lowest unoccupied molecular orbital (LUMO) level corresponding to the empty π^* -band, also known as the conducting band. Most of these polymers are colored because of the strong absorption in the visible range of the spectrum related to the π - π^* optical transition [1],[33]. Conjugated polymers in their neutral form are semiconductors, but they can be made electrically conductive through doping. Doping process will be depicted later. Typical examples of conjugated polymers are polyacetylenes, polythiophenes, polyphenylenes, polypyrroles, and polyanilines, which typically contain substitutive groups along the chains to add the processibility, see Figure 1.

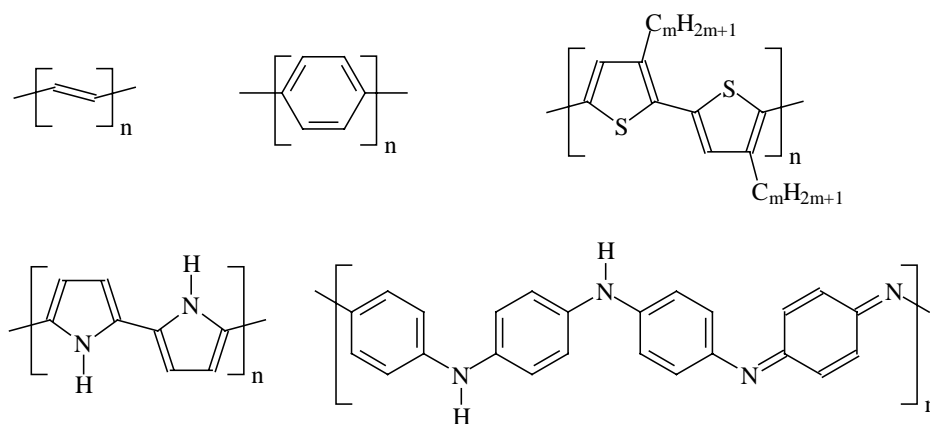


Figure 1. Examples of conjugated polymers: polyacetylene, polyphenylene, polyalkylthiophene, polypyrrole, and polyaniline.

Both undoped and doped conjugated polymers have many possible applications, and some are already in use today [34]. One of the most extensively studied applications of undoped conjugated polymers is the fabrication of polymeric light-emitting diodes [35]. These devices make use of electroluminescence, i.e. light generation by electrical excitation. Other applications of undoped conjugated polymers include corrosion prevention [1], optically pumped conjugated polymer lasers [36], plastic photovoltaic cells [37], polymer-based field-effect transistors [38] and stress-grading materials in high-voltage coaxial cables [39]. The last-mentioned application is especially suitable for undoped polyaniline, since it is a self-adaptive material and its resistivity depends on the electric field. It can thus suppress local increase of electric field which may occur in the areas of imperfections and defects of various types on the conductor-insulator interface and which are the major cause of electric breakdown.

Doped conjugated polymers have applications as conductors, which may combine relatively high electrical conductivity, feasible mechanical properties of polymers and low price. Also there is demand for optically transparent conductors. For example, one of the two electrodes in polymeric light-emitting diodes must be transparent, and blends of camphor sulfonic acid doped polyaniline with common polymers have been

demonstrated for this purpose instead of commonly used indium/tin oxide [40]. Furthermore, organic conductors can be used in the fabrication of conductive layers, fibers and antistatic coatings. The changes of the properties taking place upon doping give rise to concepts of conjugated polymers as chemical and electrochemical sensors, gas separators and pH-optodes, i.e. devices for optically measuring pH. Some of the conducting polymers are suitable materials for microelectronics. Also conducting polymers with lower conductivity can be used as charge dissipation materials in fibers and textiles instead of very thin metal coatings. There even exist ideas of conducting polymers as low-power resistive heaters and radar-absorbing materials [33].

Self-assembly

Molecular self-assembly can take place when the attractive and repulsive forces between moieties within a molecular system are balanced. In polymers, a typical example consists of block copolymers, where two different polymer blocks are covalently bonded to each other. Here the repulsion is due to the unfavorable interaction between polymer segments of different type, and attraction follows from the covalent bonding between the different blocks. Depending on the volume fractions of the blocks, diblock copolymers form e.g. lamellar, cylindrical or spherical self-assembled structures, see Figure 2 [41]. More complicated structures are achieved if more blocks are used [42].

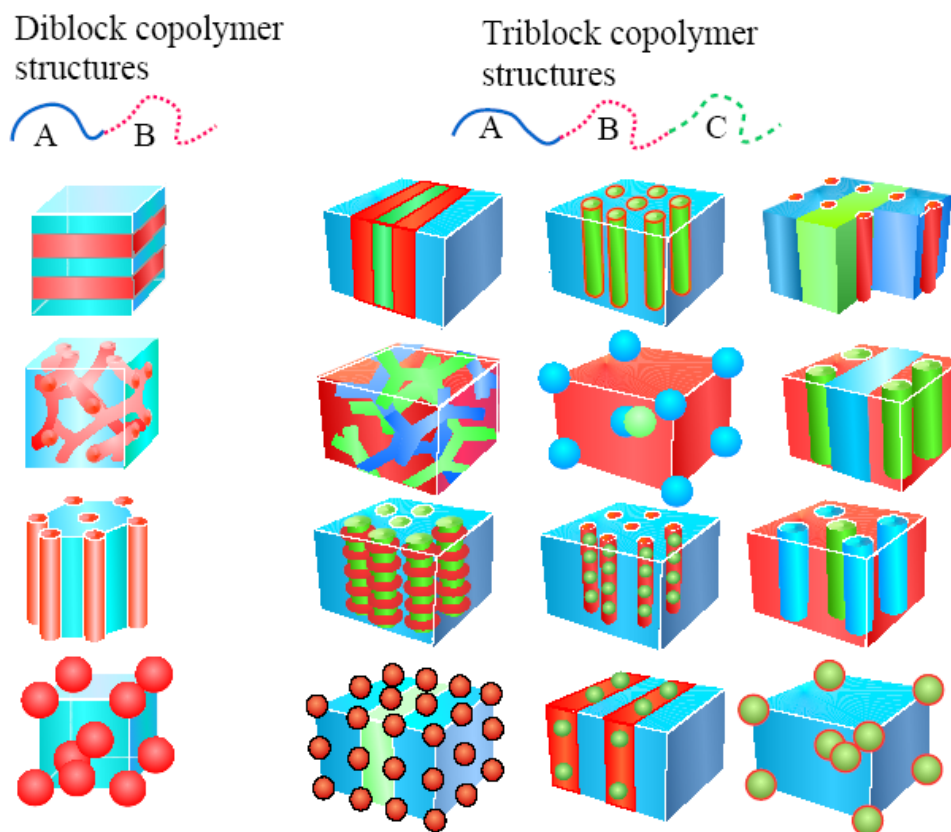


Figure 2. Diblock copolymers and triblock copolymers provide examples of self-assembled structures [41, 42].

Other examples of self-assembled polymeric structures are amphiphilic molecules attached to polymers by ionic bonds [4, 43, 44], by coordination [45, 46] or by hydrogen bonds [6, 29]. Also here the balance between repulsion (repulsion between the polar and nonpolar moieties) and attraction (bonding of the amphiphile to the polymer backbone) exists. Paper III describes comb-shaped supramolecules, where small molecules are bonded to the polymer backbone by ionic and hydrogen bondings. Further possibilities of ionic self-assembly have been reviewed by e.g. Faul and Antonietti [4] and functional materials based on self-assembly of polymeric supramolecules, especially comb-shaped supramolecules, by Ikkala and ten Brinke [6]. Comb-shaped supramolecular systems often tend to form lamellar structures, although distorted lamellar and cylindrical structures are also observed, see Figure 3.

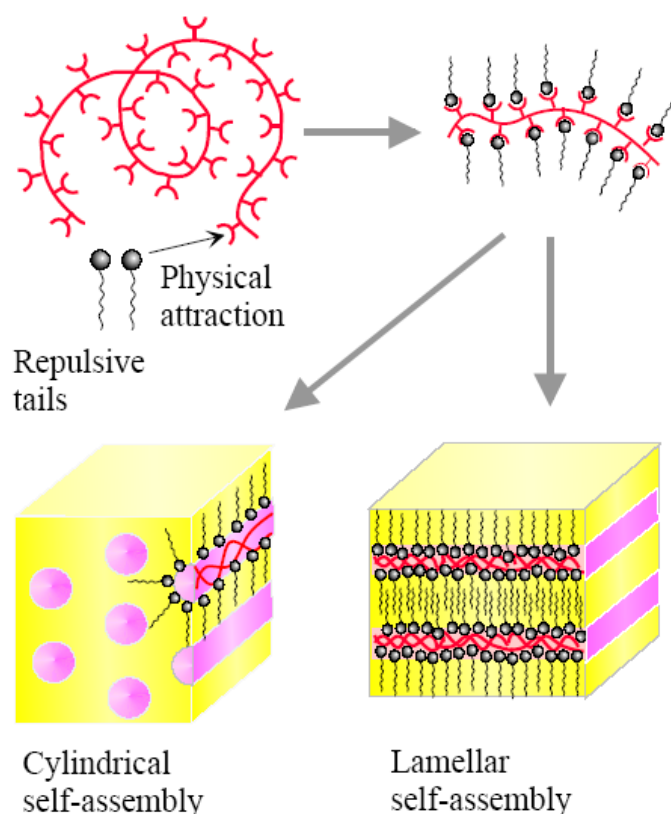


Figure 3. Examples of self-assembled structures of polymeric comb-shaped supramolecules, consisting of amphiphilic oligomers physically bonded to polymers.

Polyaniline

In the case of polyaniline (Figure 4), not only the carbon p_z orbitals but also the nitrogen p_z orbitals contribute to the π -conjugation. The emeraldine base form of polyaniline has amine and imine nitrogens in its conjugated backbone, which makes it different from most other conducting polymers, such as polyacetylene. Figure 4 also shows the oxidation states of polyaniline. The emeraldine base form of polyaniline is particularly important among the oxidation states, because it is considered to be very

stable in air and therefore such a material can be stored under laboratory atmosphere without any chemical change [33].

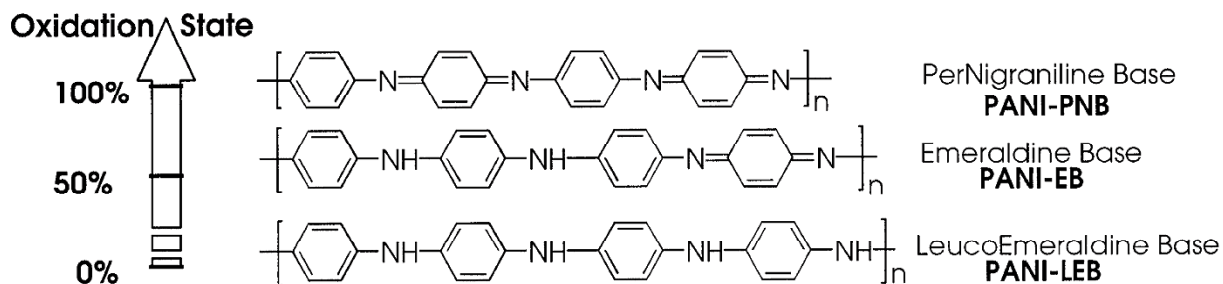


Figure 4. Oxidation states of polyaniline. [33]

Polyaniline needs to be doped in order to render it conductive. The conducting form of polyaniline can be produced either from the emeraldine base by acid-base complexation due to formation of emeraldine salt and consecutive redox-reaction [47-49] or from the leucoemeraldine base form by oxidative doping (Figure 5). The acid-base doping is more commonly used: it is performed by protonating the emeraldine base with a sufficiently strong protonic acid. Protonation also results in bond length changes as the difference between the quinoid diamine and the benzene diamine moieties vanishes when a resonance structure is formed due to an internal redox reaction (charge redistribution), leading to a conducting emeraldine salt. In the case of oxidative doping, the oxidation of neutral leucoemeraldine chain leads to radical cations. Both acid-base doping and oxidative doping lead into the same form, electrically conducting emeraldine salt.

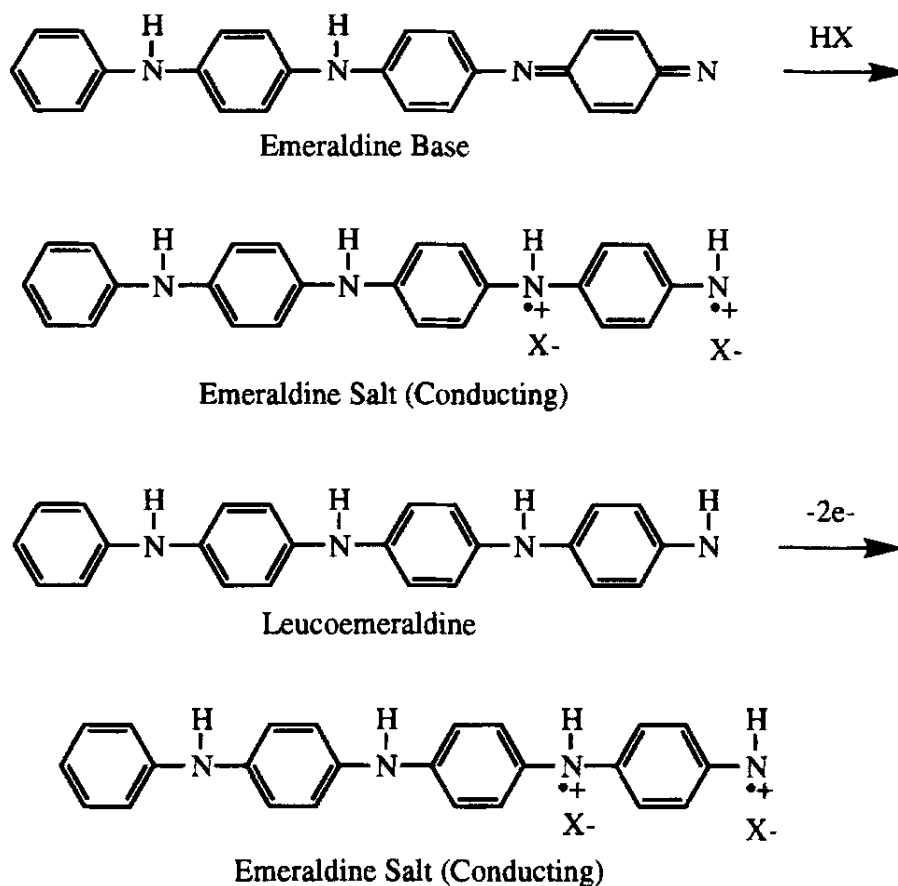


Figure 5. Acid-base doping (top) and oxidative doping (bottom) of polyaniline [50].

Doping is most homogeneously done in solution, such as in solutions of hexafluoroisopropanol [51, 52] or formic acid [11, 53]. On the other hand, doping in dispersion is also used [54, 55]. A drawback of the latter method is that solubility is achieved only when the doping proceeds in dispersed phase, which might cause more inhomogeneous doping compared to doping in solution. In the work of Adams *et al.*, the doping level was varied and the maximum conductivity was achieved with the nominal composition of 0.6 mol of dopant *vs.* mol of PANI repeat units, i.e. slight overdoping [54]. Also the aminic nitrogens may complex acids in addition to the iminic sites, thus preventing the protonation of the inner iminic nitrogens within the dispersed particles, which can be a problem in the dispersion doping. This may explain why slight overdoping is needed for actual complete protonation of the iminic sites, indicated by the conductivity maximum. In fact, Vikki *et al.* have demonstrated the enhancement of solubility of polyaniline complexes doped in formic acid solution in comparison to ones doped in some other solvents or swelling media [56].

Solubility and processibility are needed when conducting polymers are used in applications. Efforts have been made to find processing methods and especially solvents for these polymers in their conducting form. Polyaniline in its emeraldine base form is difficult to dissolve due to the intermolecular hydrogen bonds formed between the amine groups and the imine groups of the adjacent chains and π -stacking. It can be dissolved in solvents, which are capable of replacing chain-chain hydrogen bond interactions and stacking between chains by chain-solvent hydrogen bond

interactions. Typical solvents for emeraldine base are *N*-methyl-2-pyrrolidone (NMP), tetramethylurea (TMU), *N,N*-dimethylacetamide (DMAc) and hexamethylphosphoramide (HMPA) [33]. Some other solvents able to dissolve or swell polyaniline are listed in Table 1 below [57].

Table 1: Some solvents, which are able to dissolve or swell polyaniline in its emeraldine base form [57].

Solvent	CAS number	Solubility parameter δ (MPa ^{1/2})	Acidity constant pK _a
Butylamine	109-73-9	18.6	10.8
Tetrahydrofuran (THF)	109-99-9	18.6	12.3
Piperidine	110-89-4	19.3	11.1
Propylamine	107-10-8	19.7	10.7
Dimethylhydrazine	57-14-7	19.8	7.2
2-picoline	109-06-8	20.9	6.1
Pyridine	110-86-1	21.7	5.2
Tetramethylurea	632-22-4	21.7	11.2
Quinoline	91-22-5	22	4.9
Morpholine	110-91-8	22.1	8.5
Isophorone diamine (IPDA)	2855-13-2	22.2	
Aniline	62-53-3	22.6	4.6
Dimethylacetamide	127-19-5	22.7	11.6
<i>m</i> -cresol	108-39-4	22.7	10.1
Hexamethylphosphoramide (HMPA)	680-31-9	23.2	5.9
Dimethylpropyleneurea (DMPU)	7226-23-5	23.4	11.2
Benzyl alcohol	100-51-6	23.5	
<i>N</i> -methyl-2-pyrrolidone (NMP)	872-50-4	23.7	11.2
Dimethyl formamide (DMF)	1968-12-02	24.1	10.8
Ethylenediamine	107-15-3	25.3	10.1
ϵ -caprolactone	502-44-3	25.9	
2-pyrrolidone	616-45-5		
Benzylamine	100-46-9		9.2
Diethylenetriamine (DETA)	111-40-0		
Hexafluoro-2-propanol (HFIP)	920-66-1		9.3
Pyrrolidine	123-75-1		11.3
Trimethylhexanediamine (TMDA)	25620-58-0		

Conductivity and self-assembly of polyaniline

In the case of emeraldine salt, the processing was a challenge still in the early 1990s. Thin films of emeraldine base polyaniline could be cast from solution and doped after casting, but in this case the doping was easily inhomogeneous. So-called counter-ion induced processibility offered a concept to enhance the solubility of conducting polyaniline salts. Usually amphiphilic or bulky dopants are used in this approach to reduce the mutual aggregation tendency of polyaniline salt and to provide surface

activity to solvents. In 1992 Cao *et al.* used dodecylbenzenesulfonic acid (DBSA) and camphor sulphonic acid (CSA) for the acid-base complexation of polyaniline [55] and achieved solubility in many nonpolar and weakly polar solvents. CSA complexation was found to induce solubility in several different polar organic solvents. Conductivity of PANI(CSA) films cast from the solvents were surprisingly different, the highest conductivity being 300 S/cm (cast from *m*-cresol), whereas low conductivities, 10^{-4} , S/cm were obtained by casting from *N*-methyl pyrrolidone, tetramethylenesulfoxide or benzyl alcohol [58]. The conformations in solutions were also different based on ultraviolet / visible/ near-infrared spectroscopy (UV-Vis-NIR) corresponding to good and poor solvents [59].

The difference in conductivity is due to different conformations in solutions leading to different crystal structures in the solid state [60]. Ikkala *et al.* have suggested matching physical bonds between camphor sulfonic acid doped polyaniline and *m*-cresol by computational and experimental methods [61]. They conclude that in this particular system, *m*-cresol molecules may be able to twist the polyaniline rings into a more planar conformation. This increases the conjugation length, which then affects conductivity of the solid films evaporated from *m*-cresol.

Conductivity of polymeric materials typically increases as a function of temperature because of thermally activated hopping conductivity [1, 62]. For some polymeric materials, however, conductivity decreases as a function of temperature, i.e. a positive temperature coefficient of resistivity is observed [1, 54, 62-64]. This has often loosely been ascribed to more “metallic-like behavior”. One must remember that arguments related to true metallic behavior far from the cryogenic temperatures have to be used with great care as a true metallic state requires finite dc-conductivity at zero temperature, positive temperature coefficient of resistivity down to zero temperature, as well as temperature-independent spin susceptibility and linear temperature dependent thermopower [62]. Therefore, in the present context, the phrase “metallic-like behavior” in the strict sense has to be interpreted only as a shorthand notation for the positive temperature coefficient of resistivity. The positive temperature coefficient of resistivity down to the cryogenic temperatures has been observed only for few conducting polymers, really indicating metallic behavior. Such polymers include ClO₄-doped polyacetylene and sulfuric acid doped poly(*p*-phenylene vinylene) [62]. More frequently, thermally activated behavior is observed up to a finite temperature, above which the “metallic-like” positive temperature coefficient of resistivity prevails [54, 63, 64].

Positive temperature coefficient of resistivity has been reported also for PANI(CSA) films cast from *m*-cresol [65]. Another counterion-solvent pair leading to positive temperature coefficient of conductivity in polyaniline is 2-acryloamido-2-methyl-1-propanesulfonic acid (AMPSA) and dichloroacetic acid, reported by Adams *et al.* in 1998 [54]. These systems typically show “metallic-like” conductivity down to some temperature, for example 135 K for PANI(CSA) [66] and 75-115 K for PANI(AMPSA) [54]. More recently, Fedorko *et al.* have observed for camphor sulfonic acid doped polyaniline a transition from insulator-like conductivity into “metallic-like” conductivity induced by adding of plasticizers, such as triphenyl or tritoyl phosphate [67]. Here, positive temperature coefficient of resistivity is not observed, but logarithmic derivative of the temperature dependence of conductivity is reported to be negative, which is typical for metallic state.

Polyaniline complexed with amphiphilic acidic dopants leads to self-assembly in the solid state after evaporation of the solvent. For example, polyaniline fully complexed with dodecylbenzenesulfonic acid, i.e. PANI(DBSA)_{1.0}, forms a lamellar structure [68], as schematically shown in Figure 2. Ionic interaction between the polymer backbone and the surfactant counter-ions prevents phase separation, and the system can be considered as a comb-like polymeric structure. PANI doped with surfactant anions usually shows lamellar self-assembly in which stacks of polymer chains are separated by dopant anions [33, 63, 64, 69, 70]. On the other hand, also cylindrical supramolecular structures of PANI have been demonstrated [11], see Figure 2.

In paper III, the aim was to investigate the conductivity behavior of self-assembled polyaniline complexes when the PANI chains are confined within self-assembled cylinders. As encouraged by the high conductivity levels allowed by AMPSA, it was selected as the dopant, see Figure 6. To allow self-assembly, alkyl resorcinols were selected for the amphiphiles. The phenolic group consisting of two hydroxyl groups promoted sufficient attraction to PANI(AMPSA)_{0.5} to prevent phase separation. Cylindrical self-assembly was shown by SAXS (Paper III). A change in temperature coefficient of resistivity is observed upon adding plasticizing alkylresorcinol compound (Figure 7 and Figure 8). In paper III, samples exhibiting positive temperature coefficient of resistivity are referred as “metallic-like” due to their similarity to metal conductors even though no cryogenic measurements have been performed. Arguments explaining the positive temperature coefficient of resistivity can be given based on straightening of the polyaniline chains based on small-angle X-ray scattering results. This can increase the conjugation length, which in turn affects the conductivity behavior.

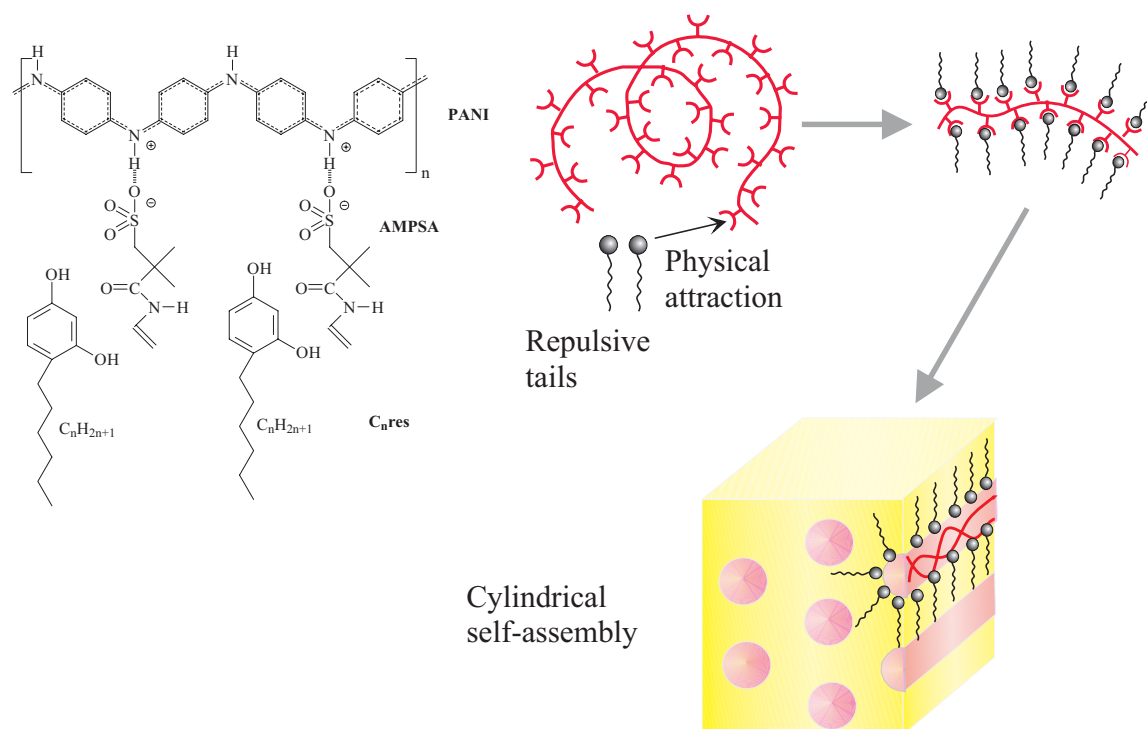


Figure 6. PANI doped with AMPSA and hydrogen bonded with alkylresorcinols, which leads to cylindrical self-assembly based on SAXS.

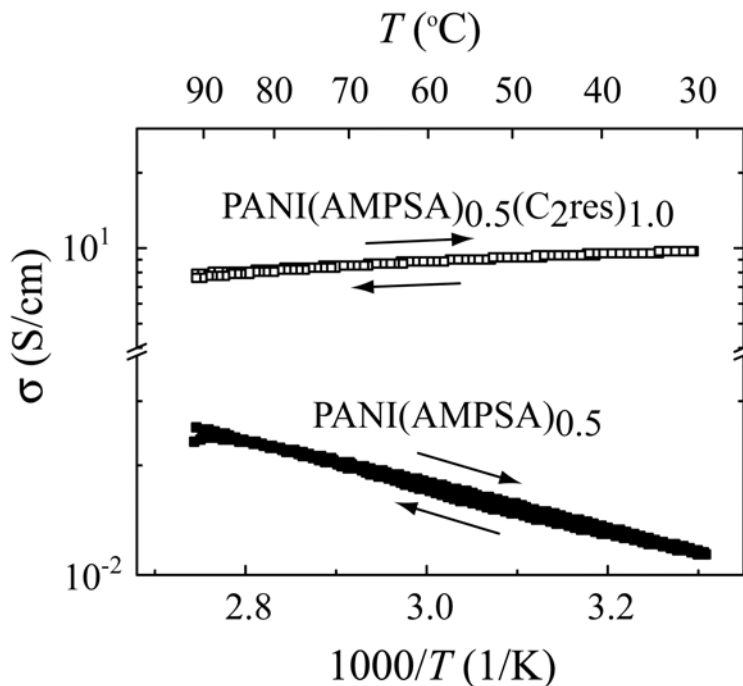


Figure 7. Electrical conductivities of PANI(AMPSA)_{0.5} and PANI(AMPSA)_{0.5}(C₂res)_{1.0}, vs. 1000/T along pressed films. The conductivities are reversible in heating and cooling cycles (Paper III).

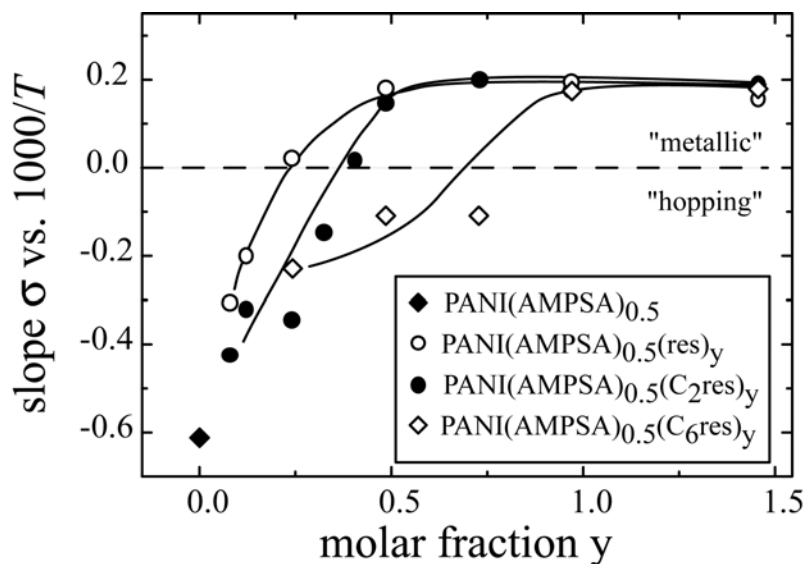


Figure 8. Slopes of conductivity plots vs. 1000/T of PANI(AMPSA)_{0.5} and complexes PANI(AMPSA)_{0.5}(C_nres)_y vs. y. Linear least-squares fitting is used to evaluate the slopes of the curves similar to those in Figure 3 (Paper III).

Corrosion inhibition using polyaniline

Some conjugated polymers capable of internal redox reactions can be used for corrosion prevention [1]. Most of the work has focused on polyaniline, but some other conjugated polymers have also been used [50]. Polyaniline was first mentioned as corrosion inhibitor by DeBerry in 1985 [71] and later it was observed to protect steel against corrosion even near a scratch where coating was damaged [72]. The mechanism of areas of bare steel being protected was concluded to be electrochemically driven, and it was observed that doping state of polyaniline and the nature of corrosion environment strongly affect the level of inhibition. Commercial polyaniline dispersions (trade name Versicon, Zipperling Kessler & Co) have been studied and a passivating oxide layer on top of steel was found to form [73].

Polyaniline coatings with additional epoxy layer have been compared with pure epoxy coatings [74]: Both neutral (emeraldine base) and doped (toluene sulfonic acid emeraldine salt) were used under corrosion environments with acidic and neutral pH values. It can be concluded that in an acidic condition protonated polyaniline protects the steel better, but in a neutral condition the nonprotonated form is more effective. It is also pointed out that high electrical conductivity is not necessarily needed for corrosion protection.

Solution processed epoxy coating with dissolved polyaniline could be feasible in corrosion inhibition, as it would combine both the good mechanical properties of epoxy and the corrosion inhibition properties of polyaniline at low cost, because lower amount of polyaniline is expected to be needed in comparison to dispersed polyaniline system. In Paper V the novel concept of dissolving polyaniline in an epoxy curing agent (Route A, a more detailed explanation in caption of Figure 9 and in Paper V) is used, and it is compared with a concept where polyaniline is simply dispersed to the composition without achieving solubility (Route B). Figure 9 and Figure 10 show that better corrosion inhibition is observed for Route A when propagation of corrosion front in immersion tests or under open circuit potential are studied.

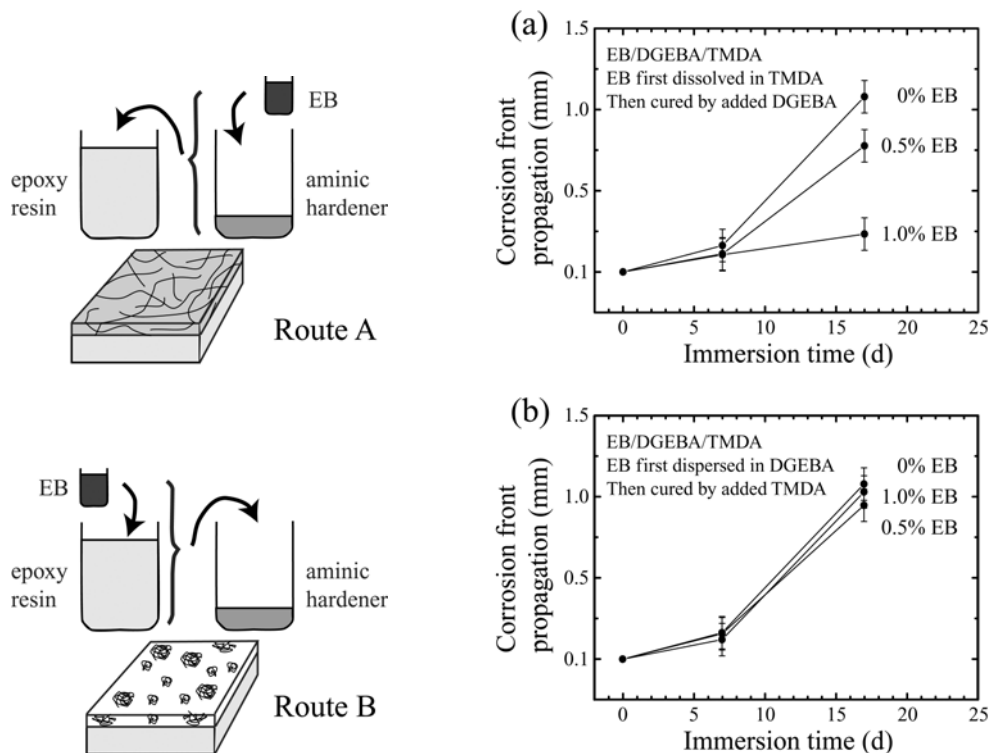


Figure 9. A simple concept based on commercially feasible materials to achieve emeraldine base/epoxy coatings with improved corrosion resistance at low weight fraction of emeraldine base. (a) Route A is based on the observation that emeraldine base astonishingly dissolves at low concentrations in trimethylhexanediamine (TMDA) which is a common epoxy curing agent. Therefore emeraldine base polyaniline (EB) is first dissolved/dispersed in TMDA and subsequently cured by adding diglycidyl ether of bisphenol-A (DGEBA). (b) Route B is more conventional where EB is first dispersed in DGEBA where no solubility takes place and subsequently cured by adding TMDA. The net compositions of EB in the final cured blends are exactly the same (Paper V). Propagation of corrosion front is studied in immersion test in aqueous 3.5% NaCl solution.

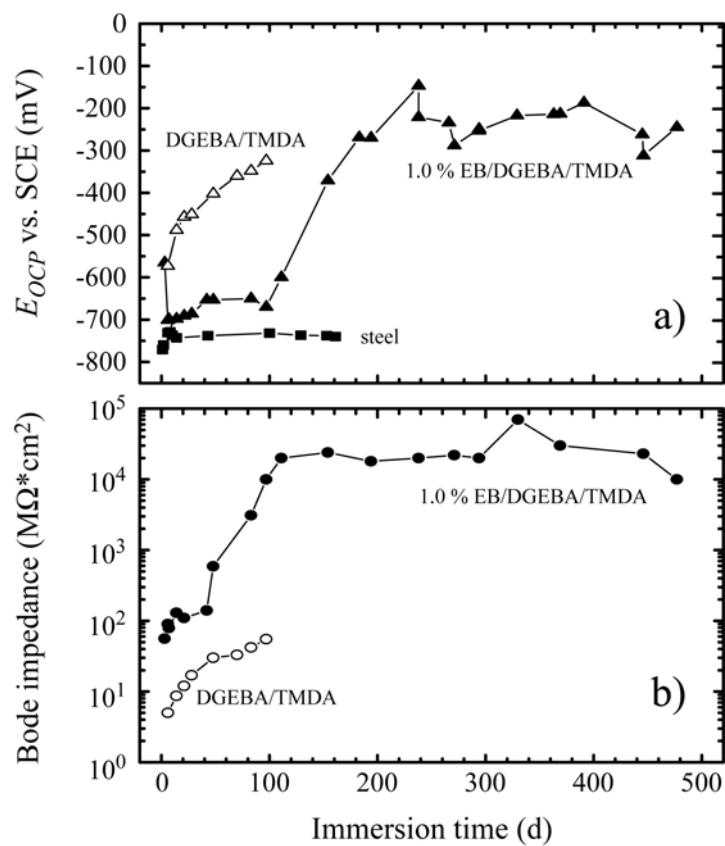


Figure 10. (a) Open circuit potential for pure DGEBA/TMDA and 1.0% EB/DGEBA/TMDA as prepared using Route A on steel in aqueous 3.5% NaCl solution. Open circuit potential for steel is also presented. (b) Total impedance at low frequency region for DGEBA/TMDA and 1.0% EB/DGEBA/TMDA (Paper V). These measurements have been performed by Anja Talo within the collaboration.

Proton conductivity

Proton conductivity attracts interest because of its scientific complexity and its importance in various technological applications and biological systems [26, 75-78]. Fuel cell membranes can be taken as an example of material research exploiting proton conductivity. Water is the most studied system, and the protonic conductivity can take place by two mechanisms (see e.g. Ref. [76]). The protonated water species (such as H_3O^+ and H_5O_2^+) can diffuse, which is denoted as the vehicular mechanism. The protons can also perform hopping in aqueous hydrogen bonded donor–acceptor chains from protonated H_3O^+ to nonprotonated H_2O , followed by their subsequent reorientation, i.e. de Grotthus mechanism [76, 79].

Below the glass transition temperature, the temperature dependency of ionic conductivity for polymeric materials usually follows the Arrhenius law

$$\sigma = \frac{A}{T} \exp(-E_a / kT),$$

where A is a constant, E_a is the activation energy and k is Boltzmann constant [80]. In practice this means that the conductivity improves at high temperatures.

Protonic conductivity of fuel cell membranes is usually based on adsorbed water [78]. However, the desirable operating temperature in fuel cells can be above 100 °C, as hydrogen-rich feedstock, such as reformed methanol, could then be used instead of pure H_2 and the catalyst poisoning could be suppressed [81]. This brings considerable interest in development of polymeric materials whose protonic conductivity is not based on water. In paper IV, such a material is constructed by protonating poly(4-vinylpyridine) with phosphoric acid to form complex $\text{P4VP}(\text{H}_3\text{PO}_4)_x$. Complexes with molar fractions $x = 1.0$ – 3.5 were prepared. More accurately, e.g. $\text{P4VP}(\text{H}_3\text{PO}_4)_3$ denotes $\text{P4VP}^+(\text{H}_2\text{PO}_4)^-(\text{H}_3\text{PO}_4)_2$. Figure 11 depicts electrical conductivities of $\text{P4VP}(\text{H}_3\text{PO}_4)_x$ complexes vs. inverse temperature.

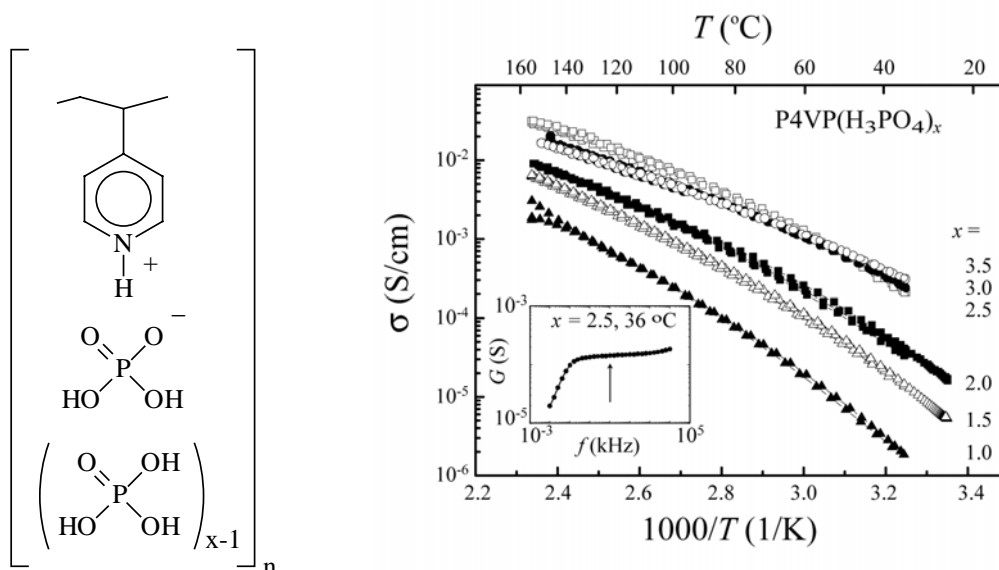


Figure 11. Electrical conductivities of homopolymer complexes $\text{P4VP}(\text{H}_3\text{PO}_4)_x$ vs. inverse temperature. As an example, the inset shows conductance G vs.

frequency f for P4VP(H₃PO₄)_{2.5} at 36 °C, and the arrow indicates the plateau conductance value near 10 kHz used for evaluating the conductivity (Paper IV).

Also polyelectrolyte – surfactant complexes are polymeric salts and have reported to allow conductivity [82], in addition of being able to self-assemble [82-85]. An example is polyacrylic acid complexed with dodecyltrimethylammoniumchloride (C12TAC), as prepared by precipitation from water and which leads to self-assembled undulated cylindrical structure after solvent evaporation [84].

In Paper VI, alkyltrimethylammonium chlorides (C_n TAC) are complexed with carboxymethyl cellulose (CMC) through acid-base reaction. Chemical compositions of the complexes and a schematical picture of the hexagonal self-assembly are shown in Figure 12. Conductivities of the bulk complexes CMC/ C_n TAC and the pure surfactants C_n TAC are shown in Figure 13, where conductivity at 27 °C vs. tail length n is plotted. Also dry samples were measured, but the results will not be represented here, however, as a general tendency the hydrated samples showed much higher conductivities than the corresponding dry samples. This suggests that absorbed water is the main source of conductivity and therefore the conductivity is expected to be protonic. For pure surfactants, increasing the tail length causes the hygroscopicity decrease, which in turn can be seen as lower conductivity values. For the self-assembled complexes, competing effects may be present: On one hand conductivity becomes lower due to longer tail causing lower hygroscopicity and on the other hand conductivity may become higher due to the better order of self-assembly.

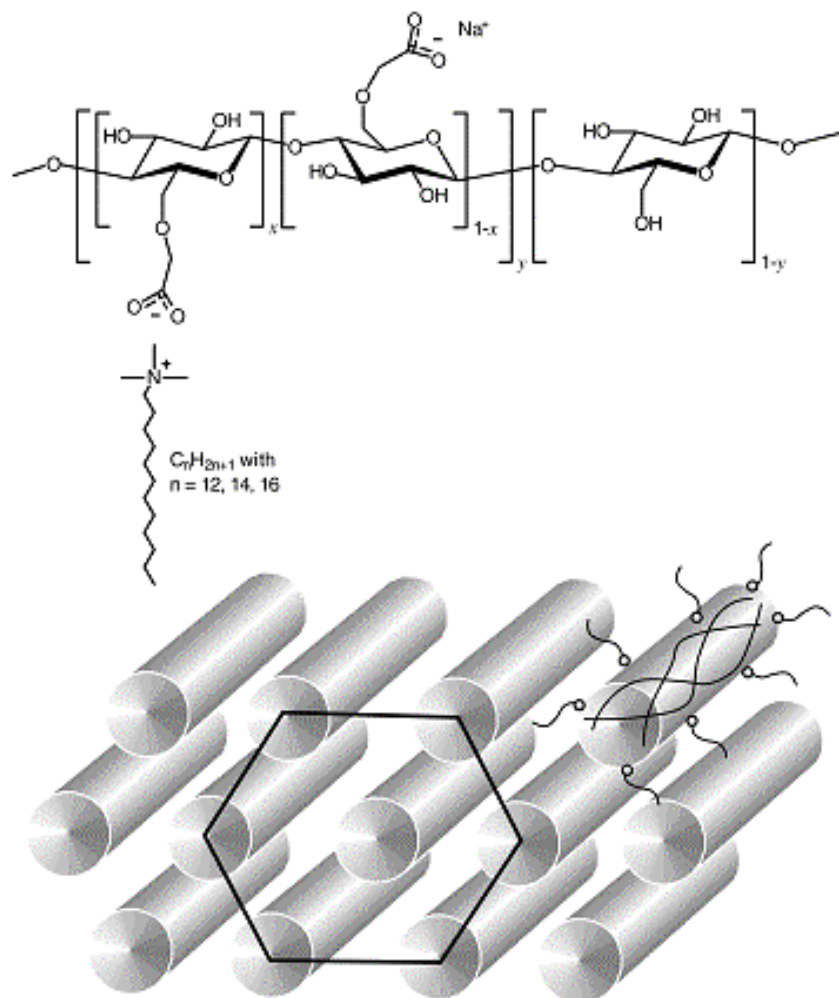


Figure 12. Chemical compositions of the complexes and a schematical picture of the hexagonal self-assembly of CMC/ C_n TAC. The bond lengths are not in proportion. In the chemical formula, y denotes the degree of carboxylic acid substitution ($y \approx 0.9$), and x the degree of complexation using the surfactants, as realized using the precipitation process (Paper VI).

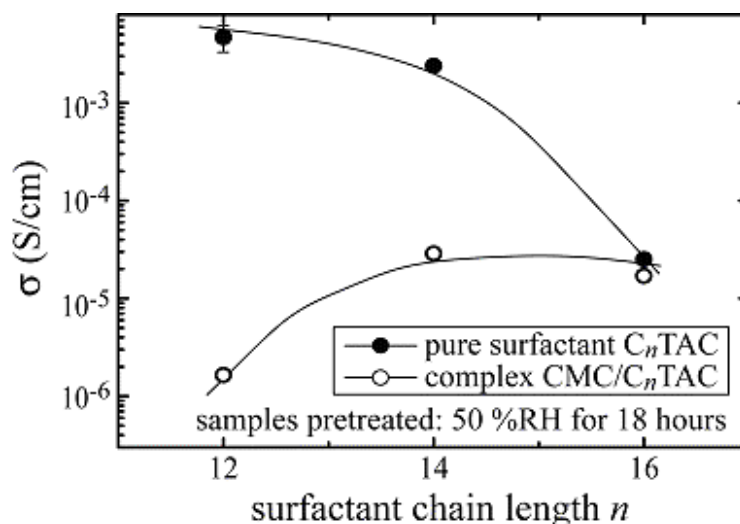


Figure 13. Bulk electrical dc-conductivities of hydrated complexes CMC/ C_n TAC and hydrated pure starting materials C_n TAC based on ac-impedance studies. Conductivity of hydrated CMC, 1.0×10^{-6} S/cm, is not plotted. The samples were pretreated under humidity of 50 %RH for 18 hours to allow moisture absorption. (Paper VI).

Local and global order in self-assembled structures

Self-assembled structures typically lead only to local structural order. A common way to induce macroscopic order in the sample is shear-flow orientation [12-19, 86]. Also electric and magnetic fields [20-25, 87], surface forces and epitaxy can be used to render overall alignment of the local self-assembled nanostructures.

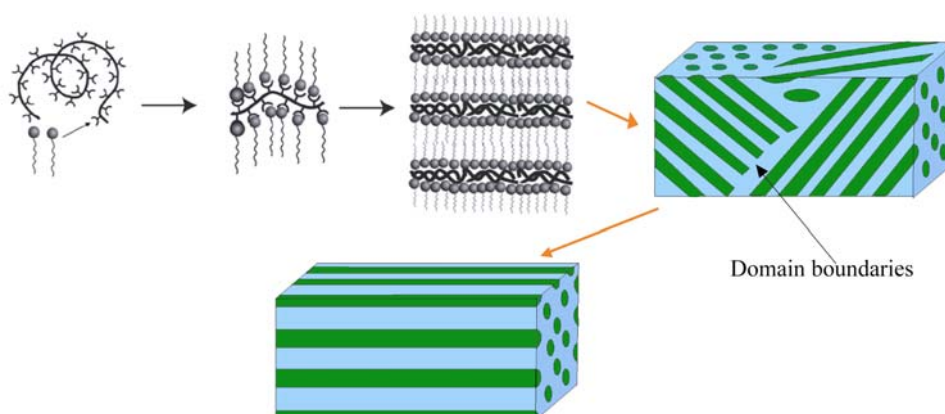


Figure 14. Comb-shaped supramolecules are formed by hydrogen bonding polymer backbone with amphiphiles. Self-assembly leads to only local domains of nanostructures. Flow can be used to align the self-assembled domains of nanostructures.

When one of the microphases in a self-assembled material is conductive, global orientation may lead to anisotropic conductivity in pieces of macroscopic size. This is illustrated in Figure 14 and Figure 15. Conductivity in the direction of conductive cylinders or lamellae is expected to be higher than in the direction perpendicular to the cylinders or lamellae. In addition of introducing anisotropy, global orientation enhances overall conductivity due to potentially decreasing the number of defects and domain boundaries [88].

A recent development has been to construct materials with self-assembled or even hierarchically self-assembled protonically conducting domains, leading to various functions and combinations of properties [6, 27, 29, 89]. In the context of fuel cell membranes, self-assembly could allow means to tailor the conductivity and mechanical properties separately. In paper IV such self-assembled and ionically conducting model material is constructed. Schematic picture of the self-assembled lamellar structure of PS-*b*-P4VP(H₃PO₄)_{2,2} and its orientation by an external flow field are shown in Figure 15 and Figure 16.

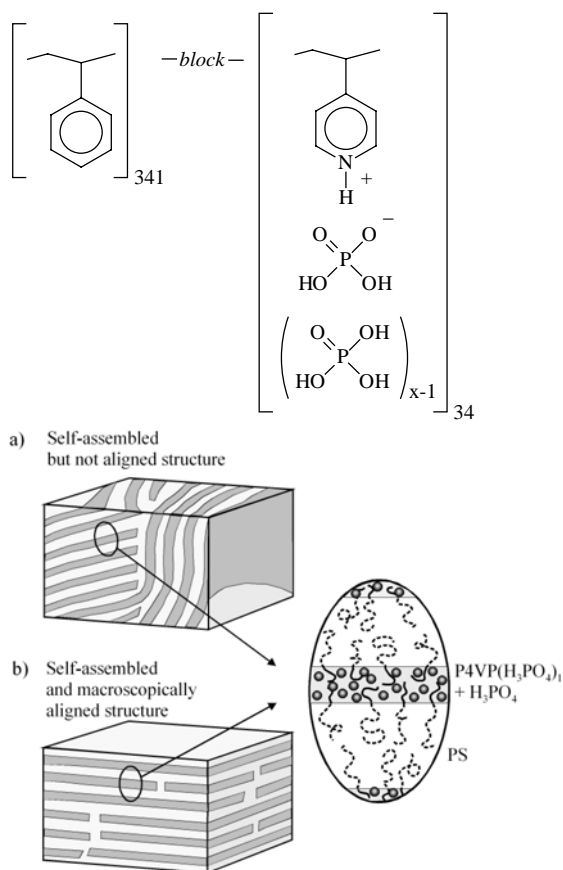


Figure 15. Schematic picture of the self-assembled lamellar structure of PS-*block* P4VP(H₃PO₄)_{2,2}. a) Self-assembly leads to local anisotropic structures but typically isotropic overall structure. b) External fields (such as flow) can be applied to align the local self-assembled structures to achieve common alignment. The structure may still have defects that cause e.g. “dead ends” of the protonically conducting channels (Paper IV).

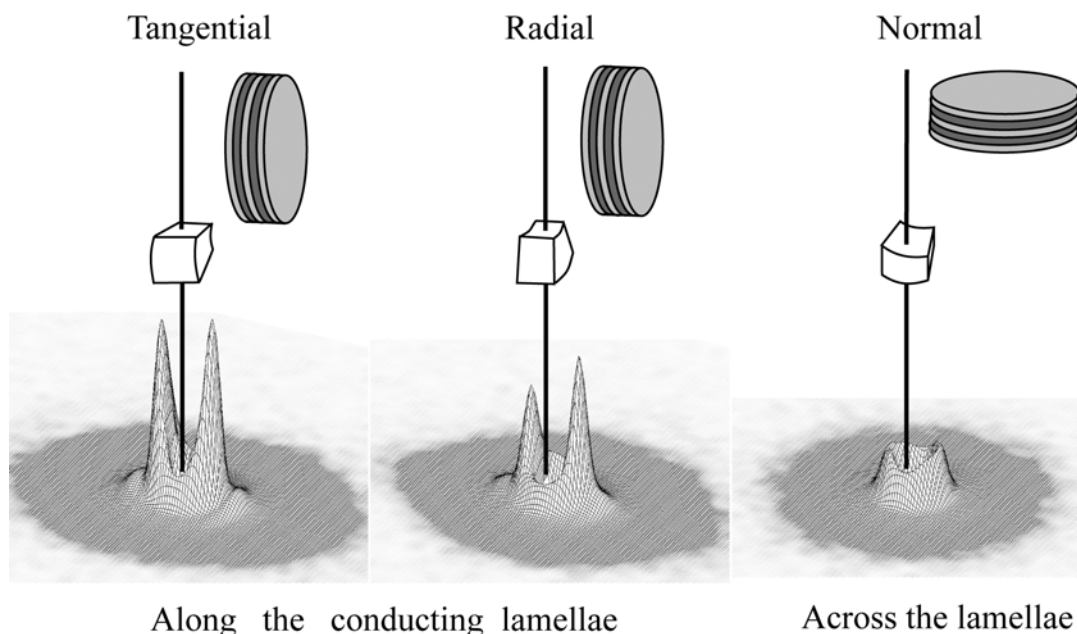


Figure 16. Two-dimensional SAXS patterns for the shear flow aligned PS-*block*-P4VP(H₃PO₄)_{2.2} in the tangential direction (along the lamellar self-assembly), in the radial direction (along the lamellar self-assembly) and the normal direction (perpendicular to the lamellar self-assembly) (Paper IV).

As mentioned earlier, achievement of global order in the cylindrically self-assembled material affects conductivity. Conductivity along the conducting cylinders becomes higher than in the direction perpendicular to the cylinders. Anisotropic conductivity behavior can be observed in macroscopic samples, as illustrated in Figure 17.

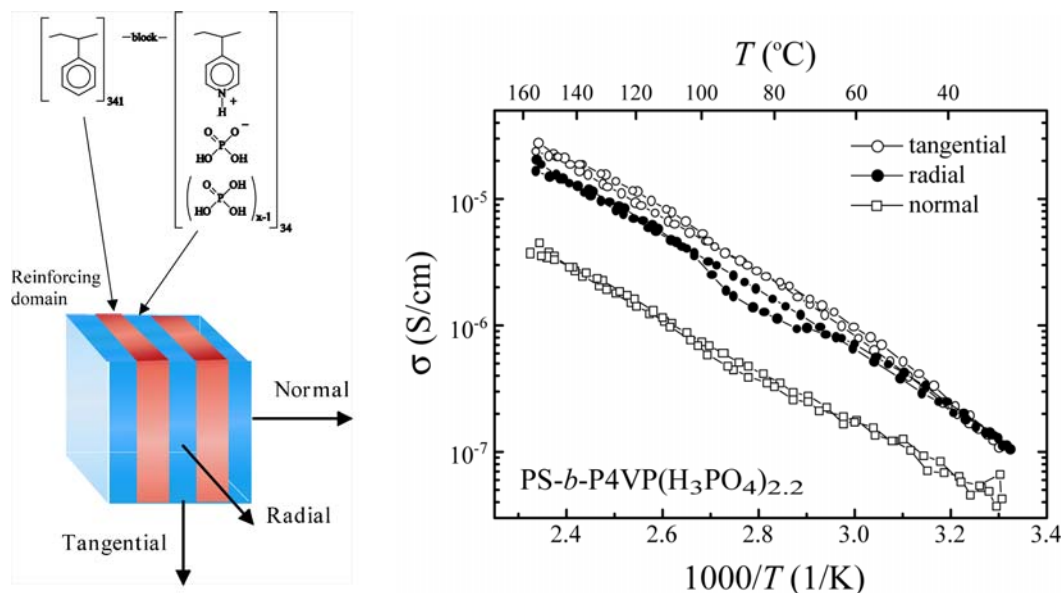


Figure 17. Conductivities of PS-*block*-P4VP(H₃PO₄)_{2.2} measured for the shear flow aligned sample in the tangential (along the lamellar self-assembly), the radial (along the lamellar self-assembly) and the normal (perpendicular to the lamellar self-assembly) directions vs. inverse temperature. Temperature is shown in the top axis. (Paper IV)

The conductivity level and anisotropy in Figure 17 are much smaller than anticipated, taken the relatively high conductivity of homopolymeric P4VP(H₃PO₄)_{2.2}, exceeding 10⁻³ S/cm at 100 °C. This implies the importance of the residual defects and “dead-ends” of the self-assembled protonically conducting nanochannels still existing after the flow alignment. Since shear flow alignment reduces the amount of defects and domain boundaries, typically conductivity of the non-aligned material is lower than any of the directions of the aligned sample [27].

Gels, percolation and critical exponents

Molecules containing several chemically reactive sites allow irreversible gelation where space-filling networks (see Figure 18) are formed in a solvent background. Gelation can be considered as a transition from a viscous fluid state (sol), which contains only finite branched clusters, to an elastic solid state (gel), which contains an infinite network [90, 91]. Related developments have taken place also in the case of reversible gelation where the junction zones of the network are formed due to noncovalent interactions, such as helical domains, microcrystalline bundles, hydrogen bonding, coordination, hydrophobic effect or some other specific interactions [30, 92, 93]. In these cases, gelation can be reversible. In dynamic rheology, the transition can be seen as a change in characteristic storage and loss moduli G' and G'' , respectively. In the sol state, $G' \ll G''$, $G' \sim \omega^2$, $G'' \sim \omega^1$, and in the gel state $G' \gg G''$, $G' \sim \omega^0$, implying transition from a viscous fluid to an elastic solid, see also Figure 19. The gel time t_g can be identified as the time where both moduli reach the same slope vs. frequency [94].

In the percolation model, the development of viscoelastic properties during gelation are described by the relative distance from the critical point $\varepsilon = (p - p_c) / p_c$, where the reaction coordinate p can be taken as the time [95]. Critical point is the moment of gelation indicated by equal slopes of the moduli vs. frequency. Near the gel point, the static viscosity diverges as $\eta_0 \sim |\varepsilon|^{-s}$ for $p < p_c$ and the static elastic modulus decreases as $G_0 \sim |\varepsilon|^t$ for $p > p_c$ which define the scaling exponents s and t [32]. Experimentally, for t values between 1.8 and 2.6 and for s values between 0.7 and 1.5 have been observed [32, 96-104]. For Δ , from slope of the moduli at gel time, $G' \sim G'' \sim \omega^\Delta$, values between 0.67 and 0.75 have been observed. Figures 1 and 2 of Paper II describe the evaluation of gelation time in practice. Theoretical models are mentioned in more detail in Paper II. As a summary, t has predicted values of 1.94 – 3 and for s the predicted values vary between 0 and 1.5 [32, 91, 96, 105, 106]. As the viscoelastic and mechanical properties are three-dimensional, the related percolation is denoted as vector percolation whereas adding ideal conductors to a network describes a scalar network [32]. In scalar percolation $t = 1.94$ [96, 107]. De Gennes first suggested that the critical behavior of scalar and vector percolation would be similar, i.e. they would have similar critical exponent t [96]. Later it turned out that they should behave differently [32].

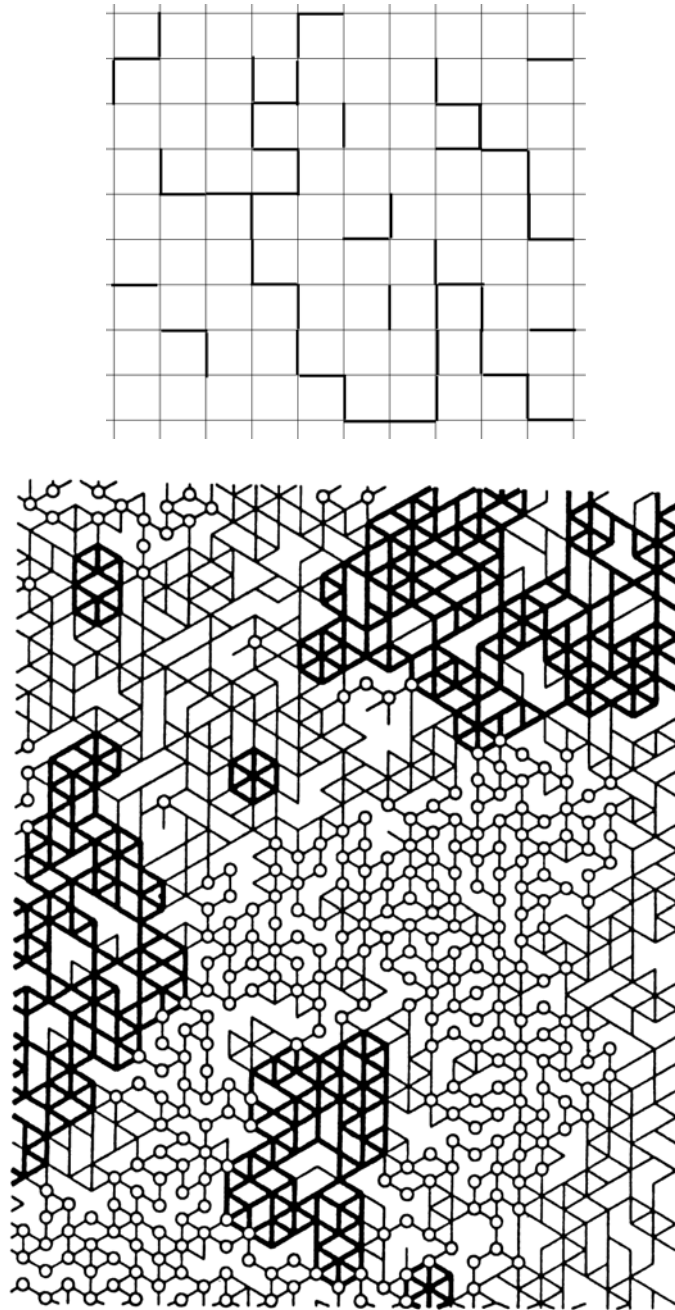
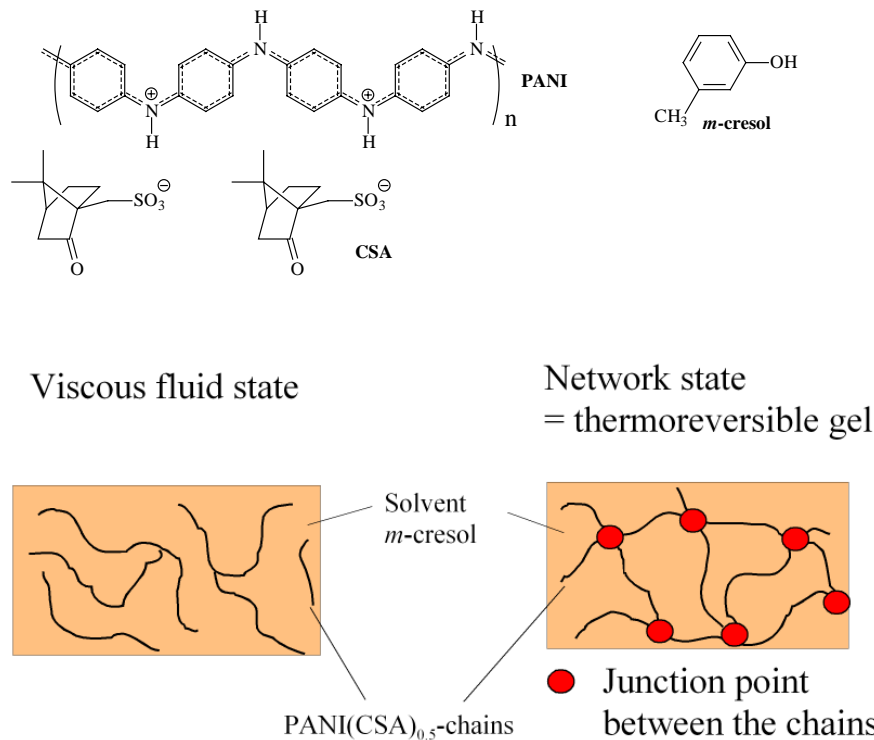


Figure 18. Schematics for percolation systems. Top: Scalar percolation [96]. Bottom: Rigidity (vector) percolation [32].

The idea of Paper II is to identify a single system, which could allow investigation of the viscoelastic vector percolation and conductivity scalar percolation in parallel and to study differences between these phenomena. In principle, conducting polymer forming a gel is a natural choice for this kind of experiment, although it is relatively difficult to identify a proper system. It turns out that the material undergoes separate viscoelastic and electrical transitions.



Viscoelastics:
 $G' \sim \omega^2$, $G'' \sim \omega^1$, $G' \ll G''$
 i.e. liquid like

Electrical conductivity
 σ expected to be small

Viscoelastics:
 $G' \sim \omega^0$, $G' \gg G''$
 i.e. solid like

Electrical conductivity
 σ expected to be larger

Figure 19. Polyaniline doped with camphor sulfonic acid was dissolved in *m*-cresol to achieve gelation.

To determine the scaling exponents, one needs to prepare master curves, which combine the rheological data of a given sample at different aging times. Axelos *et al.* [102] and Hodgson *et al.* [103] have used the following approach. The average relaxation time is given by

$$\langle \tau \rangle \sim \int_0^{\infty} G(t) dt \sim |\varepsilon|^{-s}$$

and the longest relaxation time

$$\tau_z = \frac{\int_0^{\infty} tG(t) dt}{\int_0^{\infty} G(t) dt} \sim |\varepsilon|^{-s-t},$$

where $G(t)$ is the shear relaxation modulus [93]. ω can be scaled by the longest relaxation time τ_z , and therefore the “horizontal” shift factor scales as $a_h \sim |\varepsilon|^{-s-t}$. On the other hand, $G'(\omega)$ can be scaled by the equilibrium modulus $G_0 \sim 1/J_e^0$, using

the steady state creep compliance J_e^0 . As $\tau_z \sim \eta_0 J_e^0$ and $\eta_0 \sim \langle \tau \rangle$, we conclude $1/J_e^0 \sim |\varepsilon|^t$, and G' and G'' should be scaled by the “vertical” shift factor $a_v \sim |\varepsilon|^t$.

In practice, plots of the moduli vs. ω for different aging times are shifted vertically and horizontally sufficient amount to bring them to form a continuous curve together with plots of other aging times. This of course can be done only if there is adequate amount of data sets with aging times near the gel time t_g and if the shapes of the moduli plots change sufficiently as aging time increases. The shift factors a_h and a_v needed for bringing a particular plot in contact with the others, i.e. master curve, are stored and they will later be used for determining the critical exponents s and t .

Figure 20 shows data concerning PANI(CSA)_{0.5}/m-cresol 6.5/93.5 w/w at different aging times, as combined to master curves $a_v G'$ and $a_v G''$ as a function of the scaled frequency $a_h \omega$. One can see that common shift factors can be found to combine data of different aging times to a single master curve.

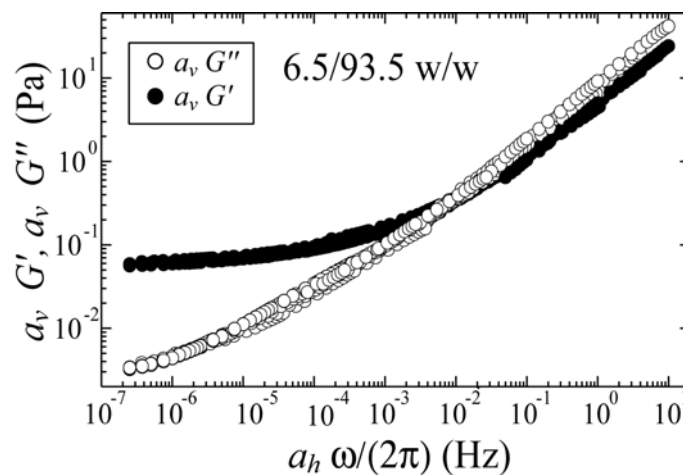


Figure 20. Viscoelastic master curves for PANI(CSA)_{0.5}/m-cresol 6.5/93.5 w/w beyond the gel point (from Paper I). The master curves contain aging times 26.7, 31.5, 36, 45, 54, 62.7, 71.5, 98, 130, 156.5 and 171 h. The gel time $t_g=24$ h. (Paper II)

Figure 21 shows logarithms of the corresponding shift factors a_v and a_h as a function of logarithm of ε . The shift factors behave smoothly and linearly vs. ε in double logarithmic-plots. The slopes of the plots equal $-t$ and $-t-s$ for a_v and a_h , respectively. Table 2 contains summary of the resulting exponents.

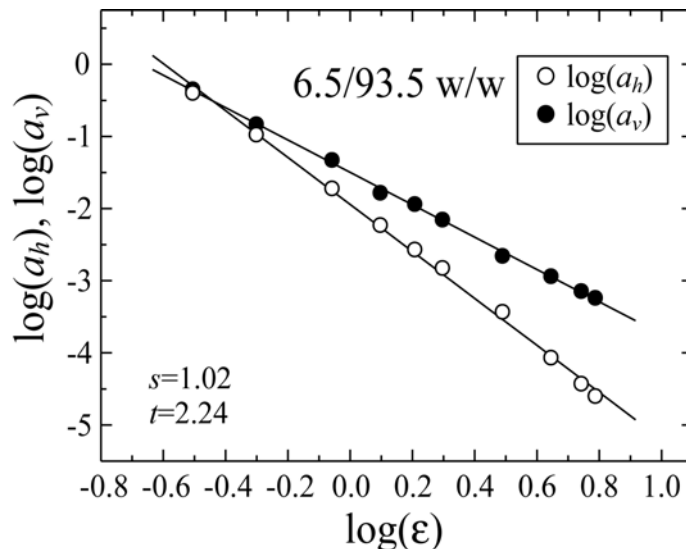


Figure 21. Shift factors used to compile the master curve for PANI(CSA)_{0.5}/*m*-cresol 6.5/93.5 w/w (Paper II).

Table 2. Viscoelastic scaling exponents observed for PANI(CSA)_{0.5}/*m*-cresol during gelation upon aging. In the concentration 8.0/92.0, the gelation was too rapid to be evaluated using the present setup and it is marked as “instant”.

PANI(CSA) _{0.5} / <i>m</i> -cresol (w/w)	gel time t_g (h)	t	s	$\Delta = t/(s + t)$ from s and t	Δ from G' $\sim G' \sim \omega^\Delta$
6.5/93.5	24	2.24	1.02	0.69	0.69
7.0/93.0	13	2.03	0.95	0.68	0.70
7.5/92.5	7.8	2.52	1.2	0.68	0.68
8.0/92.0	“instant”				

Therefore, the gelation influenced the viscoelastic behavior, which could be studied in quite detail. Also the conductivity drastically increased upon gelation (Paper III), but due to the slow changes (up to one year), sufficient data could not be accumulated to study the changes quantitatively.

Gelation for materials depicted above can be controlled by sample composition, and for certain conducting gels, gelation can be controlled by temperature. It is known that polyaniline and dodecylbenzenesulfonic acid (DBSA) form thermoreversible gels, which can be melted and after cooling they regain the gel form [56]. Amount of 0.5 mol of DBSA vs mol of repeat unit of PANI is known to fully protonate PANI and an additional amount of DBSA leads to plasticization (Figure 22) [55, 108]. Amount of DBSA between 1.5 and 3.0 mol vs mol of repeat unit of PANI leads to a thermoreversible gel, [56, 109] where PANI and protonating DBSA form a network in the additional plasticizing DBSA.

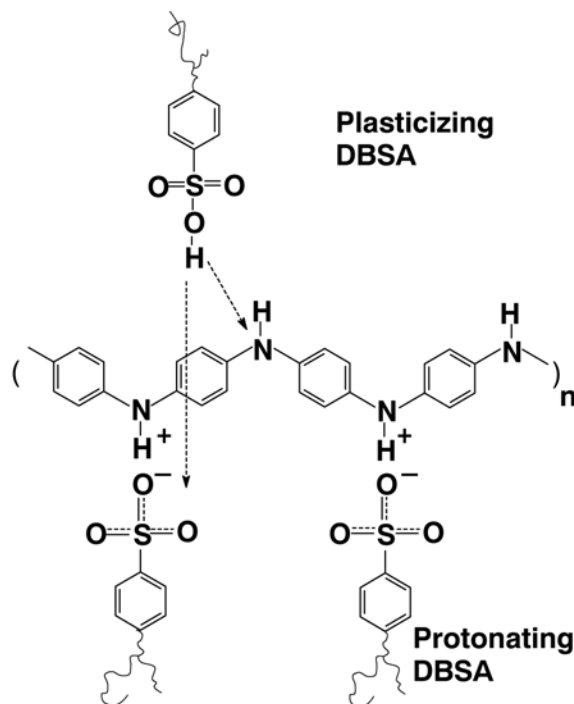


Figure 22. DBSA protonates and plasticizes polyaniline.

Formation of gels can enhance the conductivity, probably due to enhanced chain-to-chain links. In fact, thermoreversible PANI(DBSA) gels show electrical switching properties: conductivity in the gel state, below the gel melting temperature, is higher than the conductivity in the fluid state, above the gel melting temperature [109].

The above discussion on networking and gelation concentrated on liquid solvent medium. Also, it was pointed that the PANI/DBSA gel behaves as a rubbery material. In the following, we combine such material with another polymeric rubbery matrix, i.e. a thermoplastic elastomer polystyrene-*block*-poly(ethylene/butylene)-*block*-polystyrene (SEBS). This material consists of a minor amount self-assembled PS spheres within the elastic poly(ethylene/butylene) matrix and the glassy PS spheres act as “crosslinks”. The underlying hypothesis was that it could be possible to achieve conducting blends where the conductivity tolerates large deformations and extensions, in contrast to solid particle filled composites. Figure 23 shows conductivity versus elongation for two different types of elastomer blends, one system expected to consist of continuous deformable conducting network in the SEBS matrix and the other system consists of dispersed conducting powder in SEBS matrix. Indeed, even at a high weight fraction of 30 %-wt of dispersed solid PANI(DBSA)_{0.5} powder within SEBS, a small extension suffices to reduce σ drastically due to reduced contacts between the dispersed PANI(DBSA)_{0.5} particles. By contrast, for PANI(DBSA)_{2.0} in the thermoreversible gel regime, conductivity remains nearly at the original value even when the material has been stretched to 250 % of the original length, suggesting “continuous” deformable network.

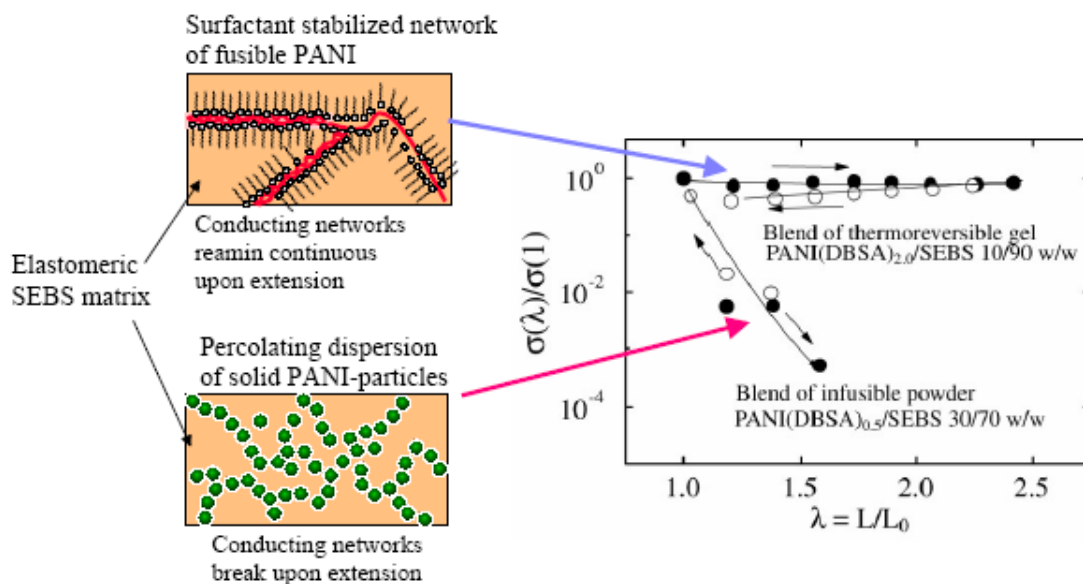


Figure 23. Conductivity vs. elongation for two different types of blends, PANI(DBSA)_{2.0}/SEBS 10/90 w/w (blend of thermoreversible gel in elastomer) and PANI(DBSA)_{0.5}/SEBS 30/70 w/w (blend of infusible powder in elastomer). (Paper I)

Conclusions

Functional polymers are scientifically interesting and can be used in many industrial applications. Internal structure of materials needs to be understood and controlled to fully use the application potential of polymeric materials. In this thesis, some examples of modifying the material properties using self-assembly, orientation of the self-assembled structures, networking and different processing methods are shown.

Conjugated polymers containing π -conjugated backbones form a scientifically and technologically important class of polymers. In their undoped form they are semiconductors, but they can be doped for electrical conductivity, and allow redox-activity, which all can lead to functional materials. One of the most important conjugated polymers in large-scale applications is polyaniline due to its economics and good stability. Polyaniline is used for applications requiring conductivity as well as corrosion inhibition.

In this thesis, conducting network structures based on acid doped polyaniline are prepared within solvent and polymer matrices, in order to investigate percolation phenomena. Self-assembled structures have been investigated to study confinement of the polyaniline chain in nanosized domains and its effects on conductivity. A concept was identified and patented to achieve a novel anticorrosion coating based on polyaniline/epoxy compositions.

In some applications ionic or protonic conductivity is preferred instead of electronic conductivity. These include e.g. fuel cell membranes or applications where colorless

conductive materials are needed. The thesis describes a model material, where the mechanical and conductivity properties can be separately tailored due to self-assembly, as well as a novel material to allow colorless antistatic paper coatings. Internal structure of materials needs to be understood and controlled to fully use the application potential of polymeric materials.

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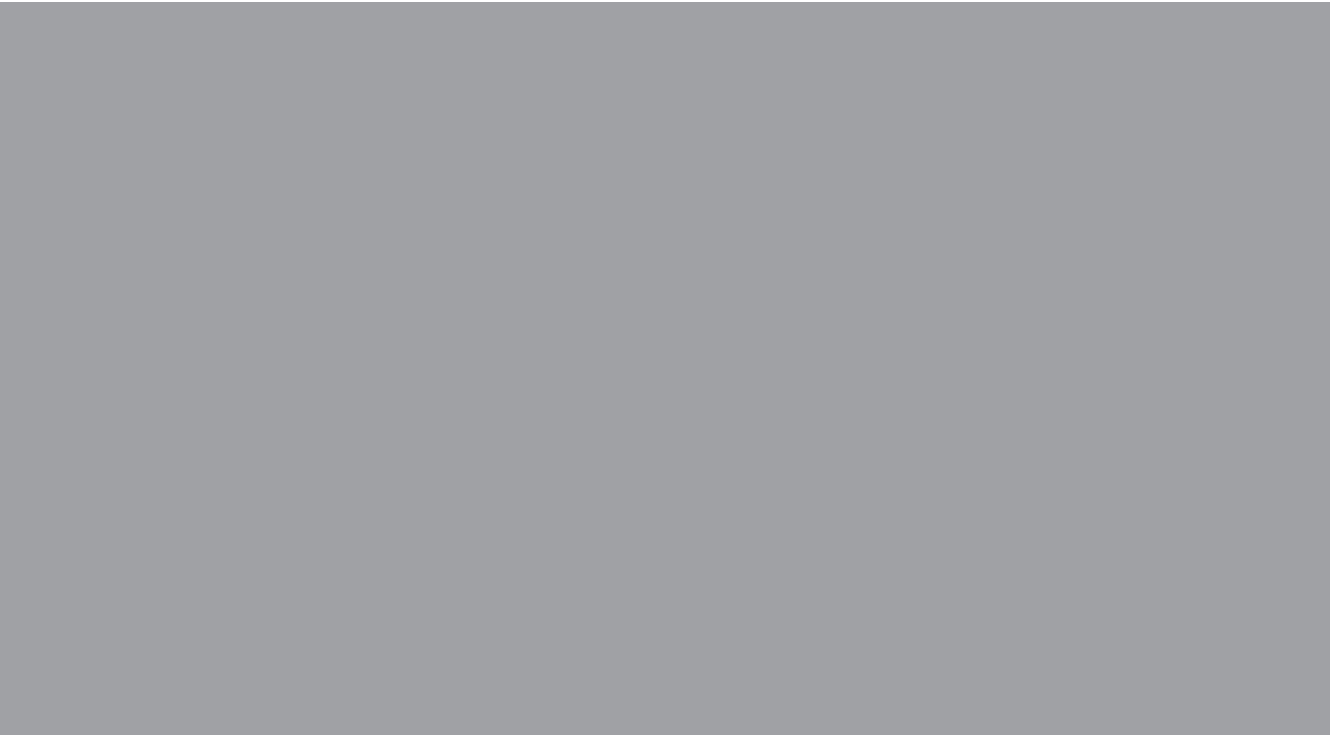
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