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FUNCTIONALIZATION OF POLYMERS WITH SELF-ASSEMBLED NANOSTRUCTURES

Harri Kosonen

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Abstract <p>In this thesis, functionalization of polymers with three different types of supramolecular self-assembled nanostructures have been examined: 1) blends of block copolymers and thermosets, 2) polymer-amphiphile systems, and 3) block copolymer-amphiphile complexes. Morphologies of complexes were characterized preferentially using small- and wide-angle X-ray scattering, and transmission electron microscopy. The effect of nanostructures on mechanical, electrical or optical properties were measured with dynamic mechanical spectroscopy, DC- and AC-conductivity, and UV-Vis spectroscopy.</p> <p>In the first example, the self-assembled diblock and triblock copolymer nanostructures (spherical, "worm-like" cylindrical and lamellar structures) were used to modify the mechanical properties of phenolic resins. Morphology of complexes depended on the weight fraction of microphase separated domain. The storage moduli at room temperature decreased slowly with increasing weight fraction of the microphase separated domain, when the phenolic matrix was continuous. The long period of the structures was of the order of 12-70 nm, depending on the molecular weights of blocks.</p> <p>In the second example, the self-assembled polymer-amphiphile complexes were used to form one-dimensional cylindrical conducting structures with the long period of 3.5 nm using conjugated polymer polyaniline. The conductivity of samples increased rapidly two orders of magnitude when the cylindrical structure was formed. The increase of conductivity is probably due to confinement of polyaniline chains within the cylinders and due to cosolvent effects of the amphiphiles.</p> <p>In the third example, the self-assembled block copolymer-amphiphile structures were used to first achieve molecularly reinforced polyelectrolyte. Complexes formed a lamellar structure, where the conductivity of "liquid-like" polyelectrolyte was decoupled from the segmental motion of the reinforcing glassy domain. Lithium salt was introduced to promote the ionic conductivity. The conductivity levels were relatively low at room temperature probably due to the Coulombic traps and grain boundaries. Finally, the hierarchical structures were used to manipulate optical properties. A high molecular weight block copolymer complexes with surfactants lead to lamellar structure with the long period of ca. 140 nm. All starting materials were almost colourless, but the complexes were predominantly blue pearlescent in reflection to an observer viewing them in ambient. The transmission and reflectance spectra revealed the formation of an incomplete photonic bandgap at ca. 460 nm.</p>			
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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 Professor Olli Ikkala and visiting Professor Gerrit ten Brinke of University of Groningen. First of all, I would like to thank them both for all the supervision and encouragement.

I wish to thank our important collaborators Professor Ritva Serimaa, Ph.D. Mika Torkkeli, Ph.D. Kaija Jokela and M.Sc. Ulla Vainio from University of Helsinki: without their experience and X-ray scattering facilities this project would not have been possible. I would like to express my thanks to Professor Franciska Sundholm and Professor Heikki Tenhu at University of Helsinki, Professor Matti Kaivola, Professor Jukka Seppälä and Ph.D. Paul Starck at Helsinki University of Technology and Lic.Sc. Tapio Mäkelä and Mr. Jukka Lappalainen at VTT Information Technology, Microelectronics. I would like to thank the former and present members of our research group, Ph.D Riikka Mäki-Ontto, M.Sc. Hannele Eerikäinen, Ph.D. Robin Ras, Ph.D. Juha Hartikainen, Ph.D. Matti Knaapila, M.Sc. Teemu Ruotsalainen, M.Sc. Olli Lehtonen, Lic.Sc. Mari Tiitu, M.Sc. Marja Vilkmán, M.Sc. Jani Turku, M.Sc. Teija Laitinen, M.Sc. Marjo Pääkkö, Dr. Nicole Volk, M.Sc. Sini Kivi, M.Sc. Sirkku Nevanpää, Mr. Panu Hiekkataipale, M.Sc. Miika Toivanen, M.Sc. Ari Laiho and M.Sc. Antti Nykänen for a nice working environment. Especially I would express my thanks to Professor Janne Ruokolainen and Lic.Sc. Sami Valkama for excellent cooperation. Our secretary Orvokki Nyberg I thank for all help.

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Espoo, September 2004

Harri Kosonen

List of Publications

- I. **H. Kosonen**, J. Ruokolainen, P. Nyholm, and O. Ikkala, *Self-Organized Thermosets: Blends of Hexamethyltetramine Cured Novolac with Poly(2-vinylpyridine)-block-poly(isoprene)*, *Macromolecules*, **2001**, *34*, 3046.
- II. **H. Kosonen**, J. Ruokolainen, P. Nyholm, O. Ikkala, *Self-Organized Cross-linked Phenolic Thermosets: Thermal and Dynamic Mechanical Properties of Novolac/Block Copolymer Blends*, *Polymer*, **2001**, *42*, 9481.
- III. **H. Kosonen**, J. Ruokolainen, M. Torkkeli, R. Serimaa, P. Nyholm, O. Ikkala, *Micro- and Macrophase Separation in Phenolic Resol Resin/PEO-PPO-PEO Block Copolymer Blends: Effect of Hydrogen-Bonded PEO Length*, *Macromolecular Chemistry and Physics*, **2002**, *203*, 388.
- IV. **H. Kosonen**, J. Ruokolainen, M. Knaapila, M. Torkkeli, K. Jokela, R. Serimaa, G. ten Brinke, W. Bras, A. P. Monkman, and O. Ikkala, *Nanoscale Conducting Cylinders Based on Self-Organization of Hydrogen-Bonded Polyaniline Supramolecules*, *Macromolecules*, **2000**, *33*, 8671.
- V. **H. Kosonen**, S. Valkama, J. Hartikainen, H. Eerikäinen, M. Torkkeli, K. Jokela, R. Serimaa, F. Sundholm, G. ten Brinke, and O. Ikkala, *Mesomorphic Structure of Poly(styrene)-block-poly(4-vinylpyridine) with Oligo(ethylene oxide)sulfonic Acid Side Chains as a Model for Molecularly Reinforced Polymer Electrolyte*, *Macromolecules*, **2002**, *35*, 10149.
- VI. **H. Kosonen**, S. Valkama, J. Ruokolainen, M. Torkkeli, R. Serimaa, G. ten Brinke, and O. Ikkala, *One-dimensional Optical Reflectors Based on Self-Organization of Polymeric Comb-Shaped Supramolecules*, *The European Physical Journal E*, **2003**, *10*, 69.

Through the Thesis, above-mentioned articles will be referred by their Roman numerals.

In addition to the articles included in this Thesis, the author is a coauthor in the following articles:

1. S. Valkama, T. Ruotsalainen, **H. Kosonen**, J. Ruokolainen, M. Torkkeli, R. Serimaa, G. ten Brinke, and O. Ikkala, *Amphiphiles Coordinated to Block Copolymer as a Template for Mesoporous Materials*, *Macromolecules*, **2003**, *36*, 3986.
2. S. Valkama, O. Lehtonen, K. Lappalainen, **H. Kosonen**, P. Castro, T. Repo, M. Torkkeli, R. Serimaa, G. ten Brinke, M. Leskelä, O. Ikkala, *Multicomb Polymeric Supramolecules and their Self-Organization: Combination of Coordination and Ionic Interactions*, *Macromolecular Rapid Communications*, **2003**, *24*, 556.
3. **H. Kosonen**, S. Valkama, J. Ruokolainen, G. ten Brinke, and O. Ikkala, *Polymeric One-dimensional Reflectors Based on Self-Organization of Comb-Shaped Supramolecules*, *Materials Research Society Symposium Proceedings*, **2003**, *775*, 147.

Author's Contribution

The results reported in this Thesis are the result of a group work carried out during years 1999-2003. The author has taken active part in the design, realization, analysis, and reporting of the work presented in this thesis. The author wrote the first versions of Articles II, III, IV, V and VI. Most part of the preparation of the complexes (except the synthesis of the starting materials), their characterization, and analysis has been made by the author. Preliminary small-angle X-ray scattering (SAXS) results of Article IV were realized by Ph.D. Matti Knaapila. The final SAXS measurements reported in Article IV were carried out as a team work at the Dutch-Belgian beamline (BM26) and those of Article VI at the beamline ID2 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

The author has also presented the results covered in this Thesis at several international conferences.

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1 Introduction

1.1 Self-Assembly

Self-assembly¹ has aroused considerable interest in the contexts of both natural and synthetic materials, as it can lead to nanoscale structures and functional or responsive materials [1-7]. To achieve self-assembly, two or more chemically different and mutually repulsive materials are required, where attractive forces prevent the macroscopic phase separation.

In homopolymers, chemically similar repeat units are covalently connected to each other and self-assembly does not take place. Diblock copolymers, where two polymers A and B are covalently connected to each other in a linear fashion, form self-assembled stable morphologies (spherical, cylindrical, gyroid, and lamellar structures) [8, 9], if the repulsion between the blocks is sufficient. The morphology depends not only on the chemical nature of polymers and the volume fraction of the polymer blocks, but also on the temperature and the number of repeat units in the polymer chain. Various other block copolymer architectures have been investigated leading to more complicated morphologies [8-13]. In many of them, "liquid crystal" moieties [9] have been incorporated in the block copolymer structure and in that case repulsion and the "aggregation" tendency are stronger and shorter blocks are needed for self-assembly.

In supramolecular chemistry, molecularly matching physical interactions are used for the structure formation (for supramolecular chemistry see Ref. [14]). Physical interactions are much weaker than the covalent bonds and the bonding equilibrium can depend on the external conditions. One example about supramolecular structures is polymer-amphiphile² complex, where the head group of amphiphile has an attractive physical interaction (e.g. hydrogen bonding [15, 16], ionic interaction [17-20], or coordination [21, 22]) with the polymer backbone. These complexes can form comb-shaped supramolecular structures in the

¹ In literature, the terms self-assembly, self-organization and microphase separation do not have precise definitions. In this Thesis we use the terms self-assembly or microphase separation to mean reversible and cooperative assembly of components into ordered nanoscale structures. In Articles I-VI we used the term self-organization instead of self-assembly. On the other hand, self-organization is used for dissipative structured materials, which require continuous energy supply (e.g. biological systems).

² Amphiphiles are molecules, which have a polar head group and a non-polar tail. Amphiphiles can form self-assembled structures in bulk and in selected solutions. Surfactants, on the other hand, are water-soluble amphiphiles.

solid state, see Figure 1. Depending on the mutual strengths of the physical attraction and repulsion (e.g. alkyl tail), three situations are possible; 1) The attraction is too weak compared to the repulsion and the polymer and the amphiphile macrophase separate; 2) The repulsion is too weak and the polymer and the amphiphile form homogenous mixture (solution) without self-assembly; 3) The repulsion is strong enough to lead to "microphase separation" of the alkyl tails, but the attraction is sufficient to prevent macrophase separation. In the last case, self-assembled structures with the long period of ca. 2–6 nm are formed, where the alkyl tails of the amphiphiles segregate into one domain and the polymer backbones together with the polar head groups into another. Polymer-amphiphile complexes usually form lamellar or cylindrical morphologies, but in some cases more complex structures are formed [20, 23]. The length and the number of side chains and stiffness of the polymer backbone affect the structure formation, but the prediction of morphology is, however, difficult. Self-assembled supramolecular structures can also be obtained without long alkyl side chains using e.g. liquid crystalline moieties [24-26].

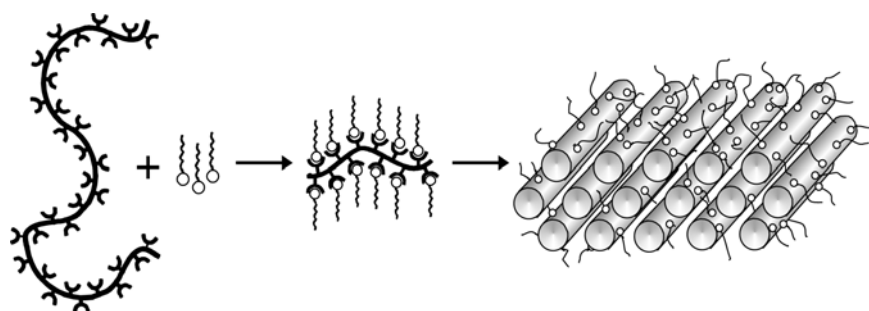


Figure 1. Schematic presentation of the polymer-amphiphile complex. The amphiphilic molecules are physically bonded (e.g. hydrogen bonding, ionic interaction or coordination) to the homopolymer backbone and self-assembled structure with the period of 2–6 nm can be obtained, depending on the mutual strengths of the attractive and the repulsive forces. Cylindrical morphology, in which polymer backbones are surrounded by alkyl tails, is shown here as an example, but a lamellar structure has been more commonly observed for polymer-amphiphile complexes.

The self-assembly of polymer-amphiphile complexes can be combined with diblock copolymers, which leads to hierarchy of structures, i.e. structure-*within*-structure (Figure 2), taken that one block has an attraction with the amphiphile and the other block has not [5, 27]. The self-assembly now takes place at two length scales, where the long periods of the block copolymer and the polymer-amphiphile complex are 20–100 nm and 2–6

nm, respectively. The morphology depends on several parameters: the volume fraction of domains, the degree of complexation, the alkyl tail lengths of the amphiphiles, and temperature. The low molecular weight amphiphiles can also be regarded as selective solvent or plasticizer due to their specific interaction. This can lead to faster structure formation and better local structures, when mobility of chains increases.

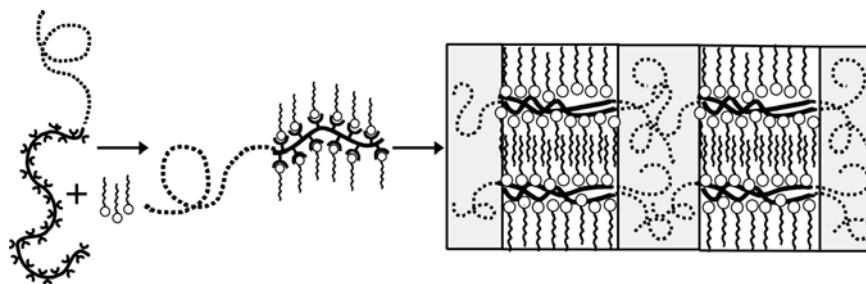


Figure 2. A schematic presentation for a hierarchical self-assembly, i.e. structure-*within*-structure morphology based on a block copolymer and amphiphiles. The long periods of the block copolymer structure and the polymer-amphiphile complex are typically 20–100 nm and 2–6 nm, respectively.

1.2 Self-Assembly Enables Nanotechnology

There are two general approaches to obtain nano-scale patterns, i.e. the "top-down" method (lithography) and the "bottom-up" method (self-assembly). Lithography based methods have their own advantages, such as well-defined long range order and possibility to locate the structures on exact positions on the substrates, but they are "restricted" to two dimensions unless considerably effort is paid for the manufacturing. In addition, it may be challenging to obtain very small structures purely based on lithographic methods, unless radiation of very short wavelengths is used. Self-assembly aims to achieve spontaneous structure formation within the matter, based on competing attractive and repulsive interactions. This enables to achieve new properties and functionality [3, 5-7, 28]; such as optical, electrical or mechanical properties, nano-objects, nanomotors, porous membranes, or high-density information storage media.

There seems to be a difficult length scale between the "top-down" and "bottom-up" approaches, i.e. the mesoscale at ca. 50-200 nm. An inherent problem related to the "bottom-up" concepts is that they easily lead to well-controlled local structures, but domain boundaries may remain. Structural difference between single crystalline and polycrystalline

materials can be regarded as an analogue. The length scale in crystals is of the order of 0.1 nm whereas in the self-assembly it is typically one to three orders of magnitude larger. The defects and domain boundaries in self-assembling materials can at least partially be reduced by applying additional fields, such as flow, magnetic and electric fields, temperature gradients and surface interactions.

Block copolymers and amphiphiles can make self-assembled nanostructures both in bulk and in solutions and mixtures. Due to this ability, block copolymers and amphiphiles have been used as structure-directing agents in the composites of organic or inorganic materials [29]. The templates, i.e. block copolymers or amphiphiles, can be removed afterwards partly or completely leading to porous materials [30-36], nano-objects [36-43] or dots [44-46], with a small variation in size and large surface area.

Noncentrosymmetric [47] and photonic bandgap materials (see Chapter 5) have been constructed using block copolymers and colloids. In the latter systems, well-defined periods at optical wavelengths with high refractive index contrast are difficult to obtain and additional orientation to suppress the defects, and the incorporation of inorganic additives to increase the dielectric contrast is needed. Some examples will be also presented in the beginning of Chapters 3-5.

1.3 Outline of this Thesis

Aim of this Thesis has been to demonstrate that the nanostructures of self-assembled supramolecules based on homopolymers, block copolymers, and amphiphiles can be used to modify material properties, such as mechanical (Articles II and VI) or electrical (Articles IV and V) properties. It will be also shown that these concepts can even lead to new properties, like optical (Article VI) properties, which was not observed in any starting materials.

The logic in the studies has been the following: First of all we have analysed the structure and interactions in the system and finally we have characterized how this structure affects on selected macroscopic properties (the mechanical properties, the conductivity or the optical properties).

In Articles I and III we describe two routes for self-assembled cross-linked thermoset blends where an attraction between cross-linkable phenolic resin and one block of the block copolymer enables the nanoscale structures after curing. We also analyse the effect of these structures on the thermal and the mechanical properties (Article II).

In Article IV we study the self-assembled structure of a conjugated polymer. We analyse the effect of structure formation on the conductivity

at the macroscopic scale. In Article V we investigate possibility for a molecularly reinforced polyelectrolyte where ionically conducting ethylene oxide side chains containing Lithium salt, are physically bonded to one block of the block copolymer, whereas the other domain is glassy.

In Article VI we represent the high molecular weight block copolymer-amphiphile complexes with structures at two length scales. The selective interaction of amphiphiles with one block of the block copolymer enables the long period to be comparable to optical wavelengths, leading to the appearance of an incomplete photonic bandgap at specific wavelengths.

Chapter 2 presents the materials used in this Thesis. In Chapters 3–5 the results of Articles I–VI are represented and discussed with a short introduction to the work done in the field. Final conclusions and some future aspects are presented in Chapter 6.

2 Materials

The complexes used in the Articles were prepared after the following procedures. The components were separately dissolved in a common solvent, and the clear and homogenous solutions were combined at ratio, which corresponds to the aimed composition of complexes. The solvent was evaporated and the samples were finally dried in a vacuum oven. For more detailed description of the sample preparation see Articles I–VI. The abbreviations of the materials used in this Thesis are listed in Table 1.

Table 1. Abbreviation of materials used in the Thesis.

Material	Abbreviation
camphorsulfonic acid	CSA
dodecylbenzenesulfonic acid	DBSA
(ethylene oxide)sulfonic acid	EOSA
hexamethyltetramine	HMTA
4-hexylresorcinol	Hres
lithium perchlorate	LiClO ₄
polyaniline	PANI
poly(ethylene oxide)	PEO
polyisoprene	PI
poly(propylene oxide)	PPO
polystyrene	PS
poly(2-vinylpyridine)	P2VP
poly(4-vinylpyridine)	P4VP

Two kinds of nomenclatures for the complexes are used in this Thesis to indicate the compositions. In Articles I-II the samples are characterized as a function of the weight fraction of the microphase separated PI-block. Note that here the weight fraction roughly corresponds to the volume fraction, which is often used in the models of block copolymer self-assembly. In Articles IV-VI the amount of moles of acid or additive are compared with the moles of the reactive or interacting repeat units of the homopolymer or block copolymer. This is indicated with the degree of complexation γ . Figure 3 represents the chemical formulas and the interactions of the materials in Articles I-VI. For the characterization methods used in this Thesis, see the Articles I-VI.

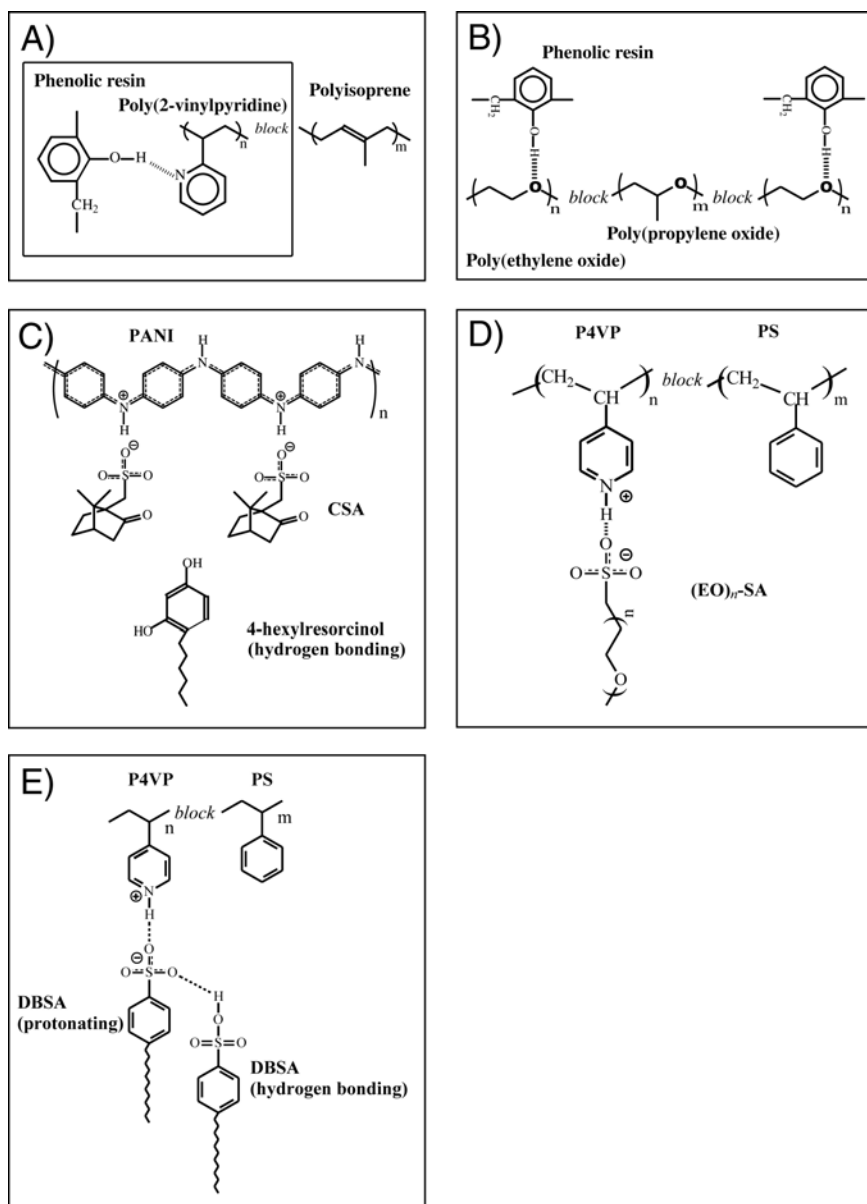


Figure 3. The chemical formulas of the materials and the interactions between them used in A) Articles I and II, B) Article III, C) Article IV, D) Article V, and E) Article VI.

3 Self-Assembly of Cross-Linked Blends of Phenolic Thermosets and Block Copolymers

Phenolic resins are commonly used thermosets in the industry [48] and they are typically hard and brittle. The mechanical properties of many thermoplastic [49-53] and thermoset [54] polymers have been modified using plasticization agents, rubbery dispersions or self-assembled nanostructures. Although the mechanical properties are largely dominated by the continuous domain, the microphase separated morphology, block copolymer architecture, deformation mechanism, and especially the interface structure and strong adhesion between domains are important. In some cases synergistic properties have been found in a small composition range for diblock copolymers having a large interface width [51]. In Articles I-III, we aimed to study supramolecular self-assembled morphologies of phenolic resins and block copolymers and how these structures affected on the mechanical and thermal properties.

3.1 Background and Related Studies

Phenolic resins are small molecules ($M_n \approx 500\text{--}5000$ g/mol), which are synthesized from phenols and formaldehydes. Depending on the synthesis conditions, the phenolic resins can react directly or via a so called hardener to form three-dimensional networks [48]. Phenolic resins and epoxies are common examples of thermosets and after formation of covalently bonded network they do not melt or dissolve in solvents due to the network of “infinite” molecular weight. Uncross-linked phenolic resins, in turn, are soluble in many polar polymers due to the strong ability of phenols to form hydrogen bonds via their hydroxyl group [55-58]. Upon cross-linking, there is a tendency to macroscopic phase separation due to the entropy penalty upon forming the network. In addition, the commonly used curing at elevated temperatures reduces the number of hydrogen bonds, which also promotes macrophase separation. In some cases it has been observed that phenolic resins and polar polymers form interpenetrating networks even after curing, when the weight fraction of the solubilized polymer is sufficiently small compared to that of the phenolic resin [57].

The phase behaviour of blends of homopolymer A and block copolymer *A-block-B* is more complicated than that of the pure diblock copolymer as there is an interplay between macrophase separation and self-assembly [9, 59-61]. The molecular weights of homopolymer A and

the A-block of the block copolymer *A-block-B* affect the structure formation. When the molecular weight of homopolymer is smaller than the molecular weight of the corresponding block of the block copolymer, “wet-brush” like structure is observed potentially leading to a change of morphology. On the other hand, increased molecular weight of the homopolymer leads to a tendency of homopolymer segregation to the center of the microphase separated domains. Finally, when the homopolymer is larger than the corresponding block of the block copolymer, macrophase separation predominates [9]. The similar situation can be observed with blends of block copolymer *A-block-B* and homopolymer C, if the interaction parameters are correctly chosen [9].

Self-assembly of thermosets has been investigated recently and it is even more difficult to sketch a phase diagram for this kind of system, because the energies involved in the chemical reactions may be larger than the weak physical energies of the self-assembly. Self-assembled thermoset networks can be divided into two approaches: Curing of thermoset precursors in the presence of block copolymers [54, 62-69] and polymerization of specific surfactant assemblies [70-74]. In addition, cylindrical, lamellar and disordered structures have been demonstrated by polymerizing phenol-formaldehyde in the presence of cationic surfactants [75].

In the self-assembled thermosets, typically the low molecular weight epoxy resins have been mixed with amphiphilic block copolymers, such as poly(ethylene oxide)-*block*-poly(ethylene-propylene) [62, 63]. Before curing, the epoxy resin is miscible with PEO-*block* due to their matching polarity and therefore microphase separated structures are observed. The structures are essentially retained upon amine curing, but due to the reduced mixing entropy as the cross-linking progresses and weak interactions between the epoxy and PEO, “a wet-brush/dry-brush transition” and segregation of PEO tends to occur. The growing network, however, topologically limits the extent of the phase separation to be only local. As an effort to control the macrophase separation, block copolymers with reactive groups have been introduced [65, 66]. In addition, it has been observed that different amine hardening agents can reduce tendency for the macrophase separation [64, 67, 69]. Self-assembled structures have been obtained also with blends of epoxy resins and tri- [64, 67, 69] or tetrablock [66] copolymers or block copolymer with one crystalline block [68].

3.2 Self-Assembled Blends of Phenolic Resin and Poly(2-vinylpyridine)-*block*-Polyisoprene and their Properties (Articles I–II)

Phenols form relatively strong hydrogen bonds with pyridines [76]. The aim in Articles I-II was to use supramolecular nanostructures of amphiphilic block copolymers, i.e. poly(2-vinylpyridine)-*block*-polyisoprene (P2VP-*block*-PI), to modify the mechanical properties of phenolic resin. Morphologies of complexes were characterized using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). Figure 4 shows the TEM micrographs of the cross-linked blends of phenolic resins and block copolymers P2VP-*block*-PI, when the molecular weight of the P2VP-block was considerably larger than the molecular weight of phenolic resin before curing ($M_{n,PI} = 71,000$ g/mol and $M_{n,P2VP} = 21,000$ g/mol). The weight fractions of PI-domains in the complexes were 0.20, 0.30, and 0.40, corresponding to spherical, “worm-like” cylindrical and lamellar structures, respectively. The observed structures with increasing weight fraction of PI were quite similar to those expected for blends of block copolymer A-*block*-B and homopolymer A when the molecular weight of homopolymer A is smaller than that of the A-block.

Fourier transformation infrared spectroscopy (FTIR) was used to study interactions between phenolic resin and P2VP. It was observed that before cross-linking there exist hydrogen bonds between P2VP and the phenolic resin. In Figure 5 FTIR spectra are represented for the starting materials and one complex after the curing. Shifts in absorption bands indicate that the hydrogen bonds remain even after cross-linking. On the other hand, there were no considerable changes in the absorption peak intensities indicating that the number of hydrogen bonds has not been significantly decreased. It was actually surprising that even after curing, when the entropy of the phenolic matrix decreases dramatically, there were no observable signs for even partial macrophase separation between P2VP-block and phenolic matrix.

The effect of molecular weight of P2VP-block was investigated using block copolymer with a shorter P2VP-block ($M_{n,PI} = 30,000$ g/mol and $M_{n,P2VP} = 2,800$ g/mol). In this case phenolic resin did not swell the P2VP-block so effectively and lamellar and even inverse cylindrical structure was observed when the weight fraction of PI-domains was only 0.20. The long period of this complex was ca. 50 nm. In Figure 6 TEM micrograph for the cured complex and SAXS curves for the uncured and cured

samples are represented indicating a lamellar structure with the long period of ca. 50 nm (the weight fraction of PI-domain was 0.40).

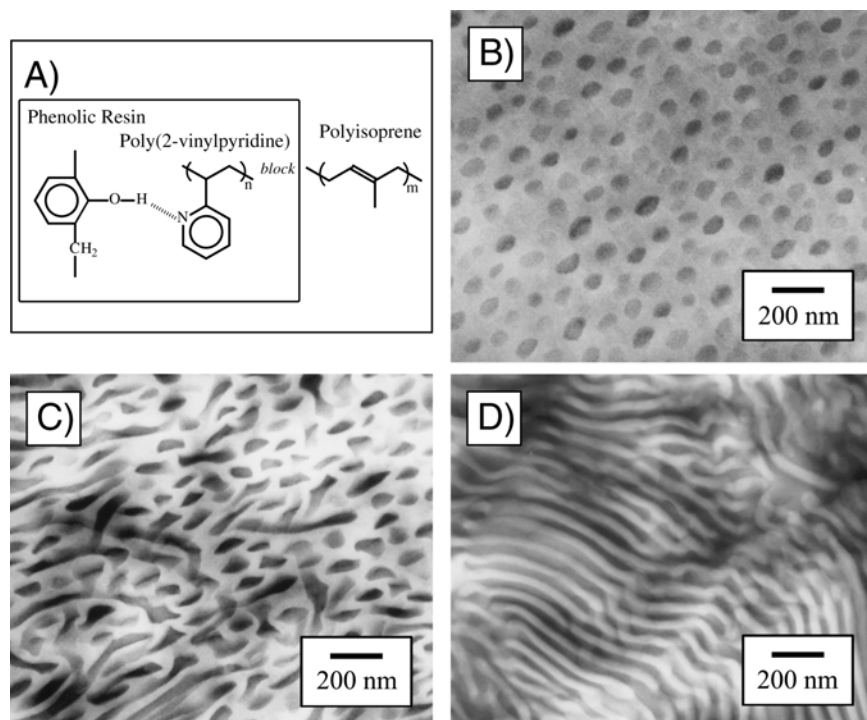


Figure 4. A) The chemical formula of the phenolic resin and the block copolymer P2VP-*block*-PI ($M_{n,PI} = 71,000$ g/mol and $M_{n,P2VP} = 21,000$ g/mol) and hydrogen bonding between them. Due to hydrogen bonds, the phenolic resin and P2VP are confined within the same self-assembled domain even after the cross-linking whereas PI forms the other domain. TEM micrographs of the cross-linked blends showed spherical, “worm-like” cylindrical and lamellar structures, when the weight fraction of PI was B) 0.20, C) 0.30, and D) 0.40, respectively. Due to OsO_4 staining PI domains show dark in the images. (TEM by J. Ruokolainen)

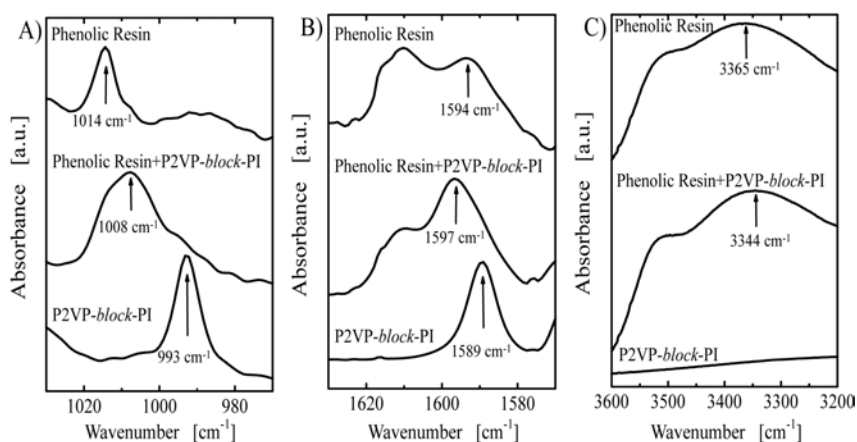


Figure 5. FTIR spectra of phenolic resin, P2VP-*block*-PI, and one of their blends (containing 0.40 of PI) after curing. Hydrogen bonding between P2VP and phenol causes shifts in FTIR bands: A) a band of P2VP shifts from 993 cm^{-1} to 1008 cm^{-1} , B) a ring stretching band of P2VP shifts from 1589 cm^{-1} to 1597 cm^{-1} , and C) a hydroxyl stretching band of hydrogen bonded phenolic resin shifts from 3365 cm^{-1} to 3344 cm^{-1} . The shoulder at ca. 3500 cm^{-1} is due to the free hydroxyl groups and it is slightly reduced in the cured blends.

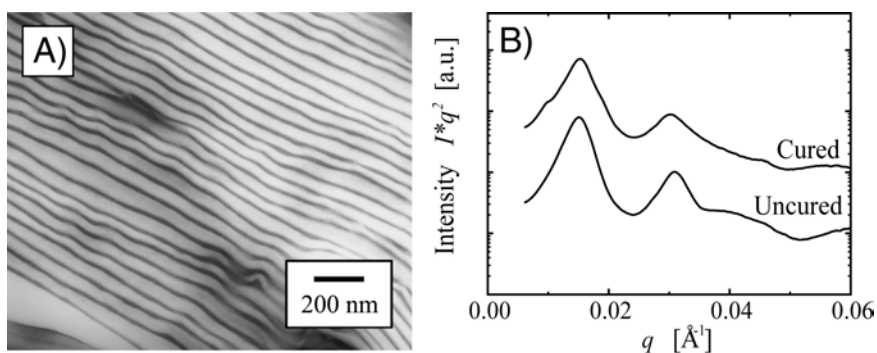


Figure 6. TEM image (cured) and SAXS curves of a blend of phenolic resin and P2VP-*block*-PI ($M_{n,PI} = 30,000$ g/mol and $M_{n,P2VP} = 2,800$ g/mol) before and after curing. The molecular weight of P2VP-*block* is only slightly larger than that of the phenolic resin before cross-linking. Weight fraction of PI was 0.40. Due to OsO_4 staining PI-domains show dark in the image. (TEM by J. Ruokolainen)

The effect of the structure, i.e. the weight fraction of PI-domains, on the mechanical and thermal properties was investigated using dynamic mechanical spectroscopy (DMA) and differential scanning calorimetry

(DSC) (Figure 7). The storage moduli of the complexes decreased only slightly when the temperature was below the glass transition temperature of PI ($T_{g,PI} = -62\text{ }^{\circ}\text{C}$). Above this temperature the storage moduli decreased slowly with increasing weight fraction of PI, when the phenolic matrix was continuous (Figure 7C). More significant decrease was observed with lamellar structure (the weight fraction of PI was 0.40). The glass transition temperature of PI was also observed with DSC at ca. $-62\text{ }^{\circ}\text{C}$.

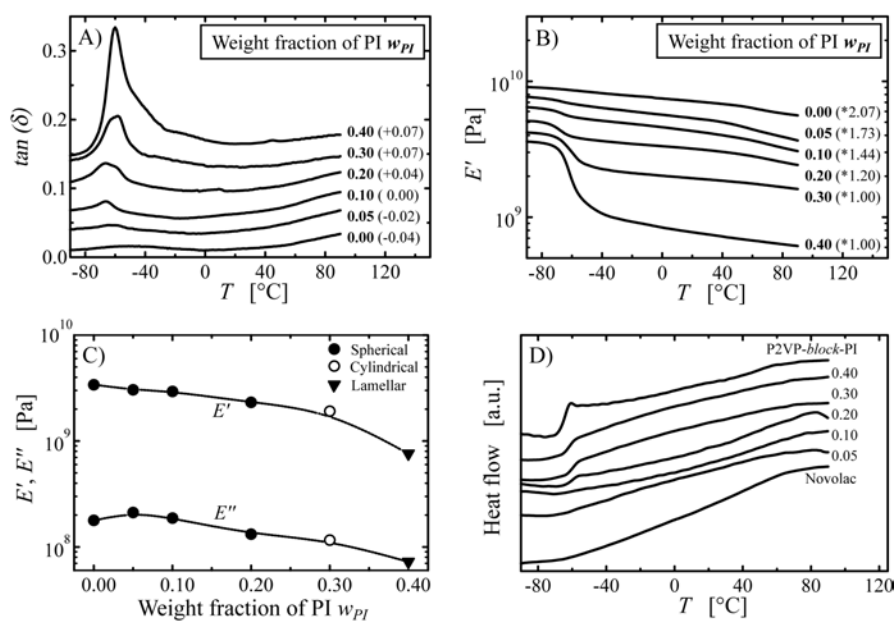


Figure 7. The effect of the morphology on mechanical and thermal properties of cross-linked blends of phenolic resin and block copolymer P2VP-*block*-PI ($M_{n,PI} = 71,000\text{ g/mol}$ and $M_{n,P2VP} = 21,000\text{ g/mol}$). A) The loss tangent ($\tan \delta$) as a function of temperature. The peak at $-62\text{ }^{\circ}\text{C}$ indicates the glass transition of PI. B) The storage moduli E' for complexes as a function of temperature. The curves have been shifted for clarity. C) E' and E'' as a function of the weight fraction of PI at the room temperature indicates that the morphology does not have a significant effect on the storage moduli, when the phenolic matrix is continuous. D) DSC curves indicating the glass transition of PI at $-62\text{ }^{\circ}\text{C}$.

3.3 The Effect of the Hydrogen-Bonded Block to the Structure of Block Copolymer/Phenolic Resin Blends (Article III)

In Article III, the effect of block copolymer architecture (i.e. triblock instead of diblock copolymer) and the length of hydrogen-bonded block to the supramolecular self-assembled structures was investigated using phenolic resin and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*block*-PPO-*block*-PEO). Phenols can form hydrogen bonds with the oxygens of PEO and PPO. Hydrogen bonds with PPO are, however, more improbable due to steric hindrance of the methyl group and we expected that the phenols form stronger interaction with the PEO-block. Three different block copolymers were used, which had almost the same length of the repulsive PPO-block, i.e. $M_{w,PPO} = 2,700$ g/mol – 3,200 g/mol. The molecular weight of PEO-blocks was varied from 400 g/mol to 900 g/mol.

The structures were characterized using TEM and SAXS (Figure 8). PPO turned out to be sufficiently repulsive to allow self-assembly in the bulk cross-linked complex. The tendency for macrophase separation increased with decreasing length of the PEO-blocks due to the decreased number of hydrogen bonds, as expected. A spherical self-assembly with a long period of the order of 12 nm was observed when the weight fraction of PEO in the block copolymer was $f_{PEO} = 0.40$ and the weight fraction of block copolymer in the complex was 0.20 (Figure 8C). Macrophase separation manifests upon curing when the weight fraction of the PEO-blocks in the block copolymers was smaller, i.e. $f_{PEO} = 0.30$ or $f_{PEO} = 0.20$. In addition, the results showed that the molecular weights of the PEO-blocks and phenolic resin have to be of the same order before curing in order to prevent macrophase separation. The chemical difference between the PEO- and PPO-blocks is smaller than that between P2VP and PI, and it is more difficult to investigate how PEO- and PPO-blocks are distributed. It is possible that wet-brush/dry-brush transition has taken place in our microphase separated sample and that the growing network topologically limits the extent of the phase separation to be only local.

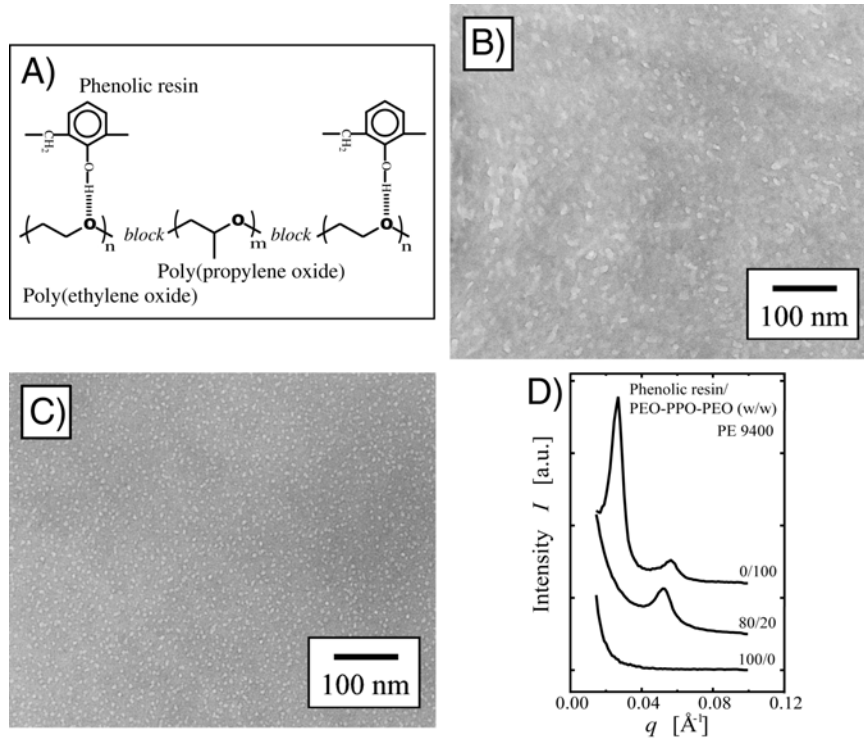


Figure 8. A) The chemical formulas of used materials and interaction between them. TEM images of the cured blends of phenolic resin/PEO-*block*-PPO-*block*-PEO, where the lengths of the PPO-blocks are approximately constant i.e. $M_{w,PPO} = 2,700 \text{ g/mol} - 3,200 \text{ g/mol}$ and the weight fraction of PEO-blocks in block copolymers was B) $f_{PEO} = 0.30$ and C) $f_{PEO} = 0.40$. D) Self-assembly in complex (PEO weight fraction 0.40) was confirmed with SAXS indicating the long period of ca. 12 nm. (TEM by J. Ruokolainen)

4 Nanostructured Conducting Systems

In Articles IV and V we investigated the effect of supramolecular self-assembled nanostructures on conductivity and mechanical properties. Two kind of nanostructured conducting systems were investigated: inherently conducting complex of polyaniline (PANI) and an amphiphile and molecularly reinforced polyelectrolyte.

4.1 Conducting Polymers and Polyelectrolytes

Conducting polymeric systems can be divided to inherently conducting, i.e. conjugated polymers (where mainly electronic excitations move) [77, 78], and ionically or protonically conducting polymers (where mainly ions or protons move) [79-83]. Inherently conducting polymers, such as polyaniline, polypyrrole, and polythiophene have a semi-rigid conjugated main chain leading to reduced solubility. Flexible side chains have been covalently [84, 85] or physically [78, 86-91] bonded to the backbone to promote processibility and solubility. Such comb-shaped or hairy rod architectures can lead to self-assembly with periodicity of 2-6 nm. In this context lamellar [85-94] and cylindrical [94] structures have been observed.

Polyaniline (PANI) in its emeraldine base form is insulating, but the protonation of PANI with a strong acid [87, 89-91, 95, 96] such as sulfonic acid, leads to an electronically conducting polymeric salt.

There are also other methods, e.g. templated self-assembly [97-101] or electrospinning [102, 103], to produce conducting objects, such as nanotubes or nanowires or low percolation in polymer colloids. The size of these structures is, however, about one or two orders of magnitude larger than the long period of the polymer-amphiphile complex.

There is a vast literature on ionically conducting polymeric electrolytes [79-83, 104-107] due to their possible application in portable electric sources. The most widely studied “salt-in-polymer” system consists of poly(ethylene oxide) (PEO) where lithium salts have been dissolved. Typically the aim is to achieve high single ion mobility of the Li^+ -cations [106, 108, 109] and to suppress the additional mobility of the anions. High molecular weight PEO is semi-crystalline whereas the conduction takes place mainly in the amorphous regions, where the chain relaxations are not hindered. Dissolution of Li-salts to PEO increase the number of charge carriers, but crystallinity and the glass transition temperature tend to increase leading to lower mobility of the ions. There has been a wealth of efforts to lower the glass transition temperature (T_g) and to suppress the crystallization of PEO in order to increase conductivity

[105, 106, 110]; Sufficiently short ethylene oxide oligomers do not crystallize, additional plasticizers, solvents and ceramic additives have been mixed with PEO; PEO can be cross-linked and the matrices can be swollen with solvents to improve conductivity and flexibility [106, 110]; Random copolymers [111, 112] or block copolymers [5, 43, 113-122] can be used, and “internal” plasticization can be accomplished by branches or combs within PEO, where the enhanced side chain relaxations improve the mobility of ions [93, 105, 108, 123-127]. Furthermore, oligomeric ethylene oxide side chains can be covalently connected to the polymer backbones to form comb-copolymers [105, 126, 128-131]. Also low dimensional conductors due to self-assembled or smectic lamellar structures have been constructed to suppress aggregation of the charges [132-138], which can lead to anisotropic conductivity.

The mechanical properties of the electrolyte must also be considered, because the increased proportion of the chain ends (low molecular weight) and additional solvent leads to softening of material. This can be overcome if the flexible side chains are incorporated within one block of a block copolymer and the overall mechanical properties could be tailored by the other block [113, 114, 118, 132, 134]. Also a rigid backbone [93, 139] or reinforcing mesogenic moieties [133] can be used.

4.2 Cylindrical Self-Assembly of Polyaniline-Salt Complexes (Article IV)

Carbon nanotubes [140] and columnar self-assemblies of other carbon nanostructures [141, 142] can show one-dimensional transport properties. In Article IV we aimed at one-dimensional conducting structures of inherently conducting PANI, where PANI chains were confined inside self-assembled cylinders. It is known that highly conducting films are achieved when PANI is nominally fully protonated with camphorsulfonic acid (CSA), i.e. PANI(CSA)_{0.5}, and when the complex is cast from a proper solvent, such as phenolic *m*-cresol [143]. “Alkyl” chain of *m*-cresol is too short to allow self-assembly and phenols with longer alkyl chain was looked for. Finding such phenols was not straightforward [144, 145]. Pentadecylphenol forms self-assembly with P4VP [15] but macroscopically phase separates from PANI(CSA)_{0.5} as the long alkyl tails cause too large repulsion in comparison to the attractive hydrogen bonds. In this respect 4-hexylresorcinol (Hres) turned out to be useful. The repulsion due to the short hexyl tails is sufficient to allow self-assembly and the two hydroxyl groups prevent macrophase separation. Hres is hydrogen bonded to PANI salt, but as there are many places where this

could take place, the exact scheme of hydrogen bonding is difficult to specify.

It was not easy to identify the solvent to prepare the $\text{PANI}(\text{CSA})_{0.5}(\text{Hres})_y$ complexes. Formic acid was used for the sample preparation and the potential tendency of the ester formation was controlled by rapid evaporation of solvent. Figure 9 show that the complexation of Hres with $\text{PANI}(\text{CSA})_{0.5}$ salt leads to X-ray scattering peaks characteristic for cylindrical structure with a distance between the cylinders around 3.5 nm. Due to the softness of the samples it was concluded that the structure could look like drawn in Figure 9C.

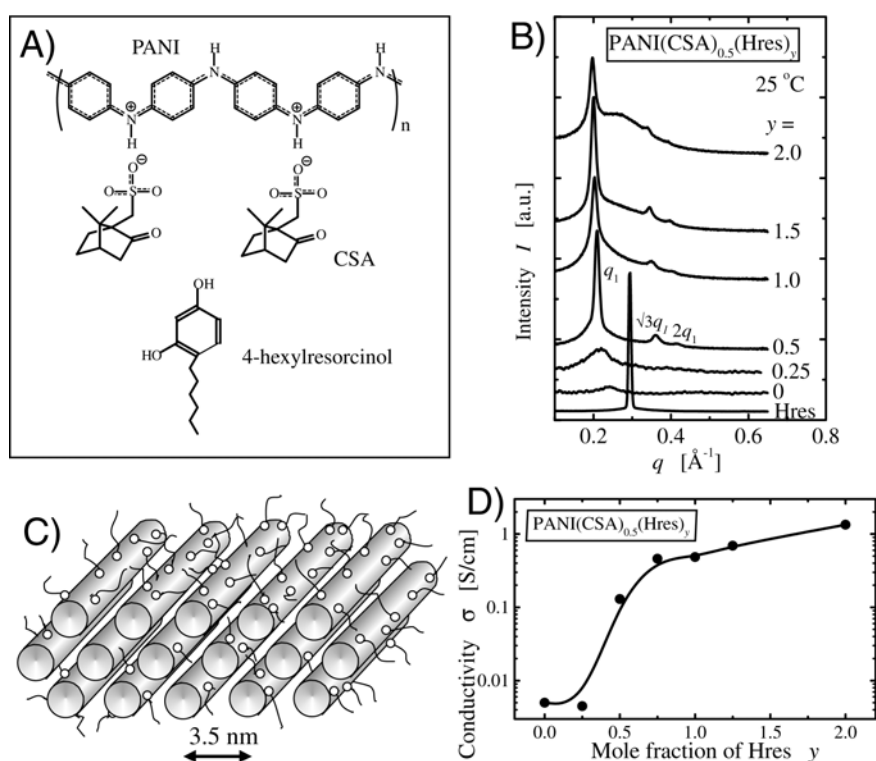


Figure 9. A) Chemical formulas of PANI, CSA and Hres and their proposed complexes. B) SAXS peaks of $\text{PANI}(\text{CSA})_{0.5}(\text{Hres})_y$, indicated formation of a cylindrical structure with a distance between cylinders ca. 3.5 nm. C) Schematics of the proposed self-assembly, where PANI backbones are surrounded by alkyl tails of Hres. D) The conductivity measurements show considerable increase of conductivity simultaneously as the cylindrical structure was formed.

Conductivity of the complexes $\text{PANI}(\text{CSA})_{0.5}(\text{Hres})_y$ were measured as a function of the complexation y . Due to the necessity to use formic

acid as a solvent, the conductivity of pristine PANI(CSA)_{0.5} film was lower than could be achieved from *m*-cresol. The conductivity increased rapidly two orders of magnitude around $y = 0.5$ when comb-shaped complex was formed and the cylindrical structure was observed. We propose that such an increase could be due to confinement of PANI-chains within the cylinders. However, certain hydrogen bonding donors are known to have cosolvent effects and lead to increased conductivity [143, 146]. It is probable that our effect is a combination of both these phenomena.

4.3 Molecularly Reinforced Polyelectrolyte (Article V)

Our interest in Article V was to combine the ionically conducting "liquid-like" polyelectrolyte of ethylene oxide (EO) oligomers with rigid mechanical properties of glassy self-assembled domains of PS. Poly(4-vinylpyridine)-blocks of polystyrene-*block*-poly(4-vinylpyridine) (PS-*block*-P4VP) were complexed with sulfonic acid terminated oligomeric ethylene oxide ((EO)_{*n*}-SA) (Figure 10) and lithium perchlorate (LiClO₄) was soaked to the P4VP((EO)_{*n*}-SA)_{1.0} domains to promote ionic conductivity. Proton transfer between P4VP and sulfonic acid group was verified with FTIR band shifts of P4VP pyridines (Figure 10B). Block copolymers with physically bonded side chains formed lamellar structures where glassy PS forms reinforcing domains and the polyelectrolyte P4VP((EO)_{*n*}-SA)_{1.0}(LiClO₄)_{*y*} the conducting domains. The long period of structures was ca. 30 nm. EO side chains have been usually covalently connected to the polymer backbone, but we expected that the physically bound side chains could have increased relaxations, which could lead to improved conductivity.

The complexes were investigated with DSC, DMA and AC-impedance measurements. The glass transition temperature of pure (EO)_{*n*}-SA was at ca. –54 °C, but it was not clearly observable in the complexes. On the other hand, the crystals in PS-*block*-P4VP((EO)₁₃-SA)_{1.0} melt at ca. 23 °C, but the starting materials did not crystallize at all.

The ionic conductivity levels remained relatively low, i.e. 10^{–7}–10^{–6} S/cm at room temperature and 10^{–5}–10^{–4} S/cm at 80 °C. There could be two reasons for the low conductivity: 1) Discontinuous conducting domains with "grain boundaries" are expected and the charges have to hop from one conducting domain with "dead ends" to another over the insulating PS domain. Later observations suggest that it may be difficult to achieve continuous conducting channels even if the self-assembled domains are aligned by flow [147] 2) The conducting domain contains a large amount

of charges due to the Li-salt and P4VP((EO)_n-SA)_{1.0} complex. These Coulombic traps could reduce the mobility of the ions.

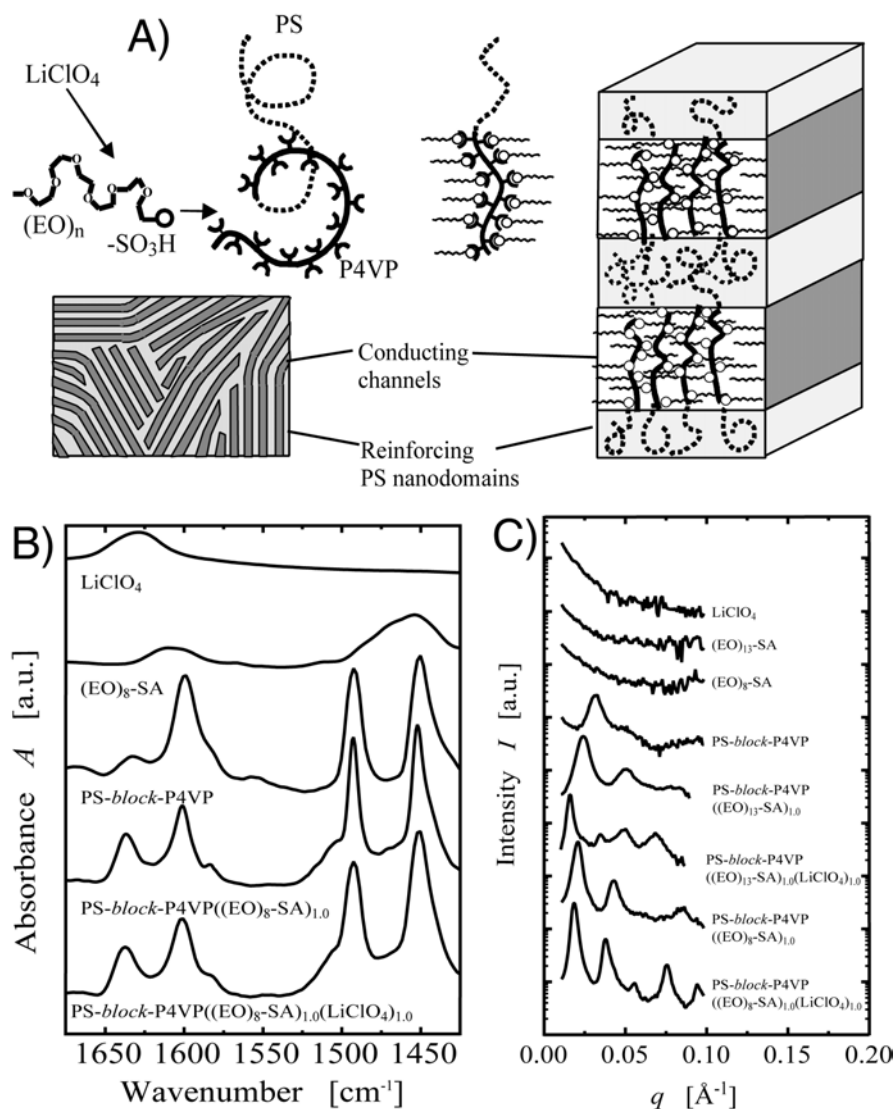


Figure 10. A) Schematic presentation for the formation of complex PS-*block*-P4VP((EO)_n-SA)_{1.0}(LiClO₄)_y. B) FTIR changes in P4VP ring stretching band indicated that protonation has taken place. C) Lamellar structure was confirmed with SAXS and the long period was ca. 30 nm.

Low glass transition temperature is favourable for high ionic conductivity, but mechanical properties, on the other hand, change when sample is heated above it. In batteries, mechanically "stable" materials are

looked for, in order to use thinner electrolyte layer. In superionic glasses [107], in turn, conductivity is decoupled from the segmental motions leading to high conductivity and good mechanical properties.

The mechanical properties of one complex and the reference materials (PS and low molecular weights PEO) were measured as a function of temperature. The storage moduli of the complexes were almost the same than that of PS at low temperatures and considerably higher than that of low molecular weight PEO at higher temperatures (Figure 11C). Glass transition and melting temperatures were observed as peaks in loss moduli curves. Our results show that the self-assembly allows decoupling of the structural and conductivity medium relaxations, when the glassy reinforcing domains and well-plasticized domains are combined. Higher conductivity and elasticity could be obtained with triblock copolymer *PS-block-P4VP-block-PS* with small PS-blocks, when P4VP polyelectrolyte forms continuous conducting domain and PS domains serve as physical cross-linking points.

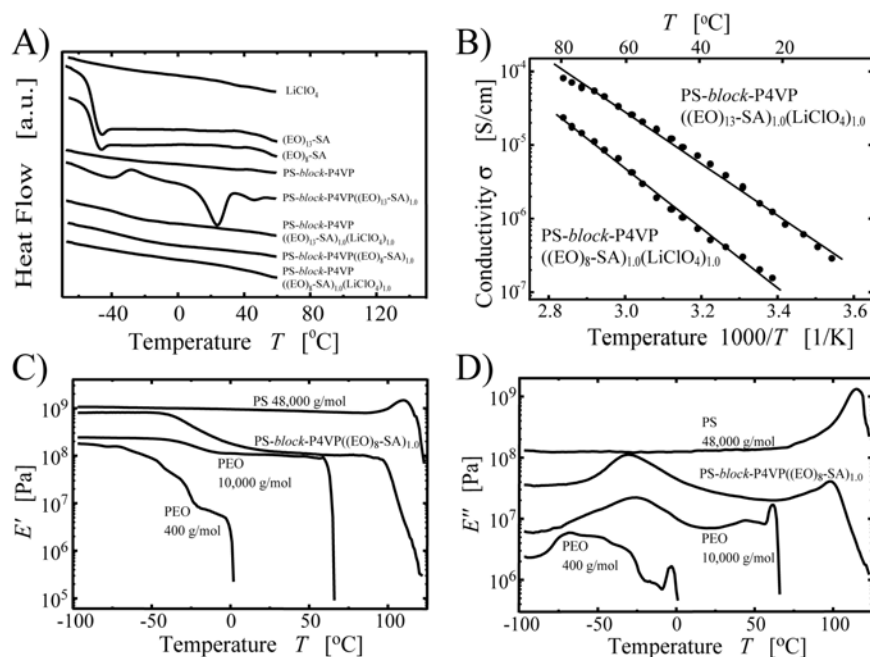


Figure 11. DSC, AC-impedance and DMA curves as a function of temperature. A) The low glass transition temperature was observed for $(\text{EO})_n\text{-SA}$ with DSC, but not for the complexes. B) Measured samples did not show any conductivity transition, because they did not crystallize. C) The storage moduli of complex remained at relatively high values up to the glass transition of the PS-domains. D) Glass transition and melting temperatures could be observed as peaks in loss moduli curves.

5 One-Dimensional Optical Reflector Based on Self-Assembly of Block Copolymers

In Article I-V we showed that mechanical and electrical properties of material can be modified using self-assembly of supramolecular structures. In article VI we demonstrate that these concepts can even lead to appearance of new properties, i.e. optical functionality, which was not observed in any of starting material. Block copolymer with repulsive side chains in one domain lead to a sufficient long period to serve as a one-dimensional optical reflector.

5.1 Photonic Bandgap Materials

The detailed manipulation of flow of light [148-151] has turned to be important in optical telecommunication. 3D periodic structures with sufficient dielectric contrast between the domains can block the propagation of light, thus leading to a complete photonic bandgap when the period of the structure equals with $\lambda/2n$ condition for the optical wavelengths (λ is the wavelength and n is the refractive index). If controlled defect structures can be combined with the bandgap, a wealth of applications in photonics is expected.

Small structures with sufficient dielectric contrast and matching periodicity with optical wavelength are usually constructed with lithographic and etching techniques. On the other hand, spontaneous assemblies of colloids [152-156], synthetic opals [157-161], inverted opals [157, 162-167], and block copolymers [32, 168-173] allow the formation of small enough structures based on competing interactions. They could offer other types of application, especially if flexibility is required, and in this sense polymers could be useful. Self-assembling systems have usually good local order, but the long-range order is poor and a complete bandgap is difficult to obtain due to the low refractive index contrast.

The long period of block copolymers can be increased up to 100 – 200 nm range just by increasing the molecular weight. Such high molecular weights would, however, lead to high viscosity, slow structure formation, and poor local and long-range order. These difficulties have been overcome by swelling the block copolymer domains with narrow molecular weight homopolymers or oligomeric plasticizers [169-171]. Also the refractive index contrast in polymer systems is often low and inorganic additives with high refractive index have been incorporated within one domain [168, 172]. Complete bandgap with self-assembled materials may

be difficult to construct, but there can be other kind of applications for them due to their unique properties compared to inorganics, such as the tuning of bandgaps [157-160] and sensors [154-156].

5.2 1D Optical Reflector PS-*block*-P4VP(DBSA)_y (Article VI)

In Article VI, high molecular weight PS-*block*-P4VP block copolymer ($M_{n,PS} = 238,100$ g/mol, $M_{n,P4VP} = 49,500$ g/mol) and dodecylbenzenesulfonic acid (DBSA) amphiphiles were used, and in their nominally stoichiometric composition PS-*block*-P4VP(DBSA)_{1.0}, the DBSA-molecules are expected to be bonded to the pyridines by protonation. Still more DBSA molecules can be added by hydrogen bonding DBSA to the sulfonates of the P4VP(DBSA)_{1.0} salts (Figure 12A). Morphology of the samples was characterized using TEM and SAXS. TEM revealed that complex PS-*block*-P4VP(DBSA)_{2.0} formed a lamellar structure with a period of ca. 140 nm (Figures 12B). The DBSA molecules have two functions; They act as constituents of the comb-shaped polymeric supramolecules and a smaller internal structure inside P4VP(DBSA)_y domains is formed due to a strong repulsion between the polar salt backbone and the dodecyl alkyl tails (Figure 12C). Perhaps more importantly, the comb-shaped architecture leads to stretching of the chains and the long period increased with increasing the mole fraction of DBSA in the complexes (Figure 12D). The DBSA molecules also serve as selective plastizicers, enabling better local structures.

All starting materials were almost colourless, but the complexes turned predominantly blue pearlescent in reflection to an observer viewing it in ambient. At the same time, the transmission and reflectance spectra revealed the formation of an incomplete photonic bandgap. The increase of the long period with increasing the mole fraction of DBSA was observed also in UV-Vis curves (Figure 13) as the reflectance peak shifted to longer wavelengths. The refractive index contrast, however, in this kind of organic polymer system is low, which explains the moderate intensity observed in the reflectance measurements.

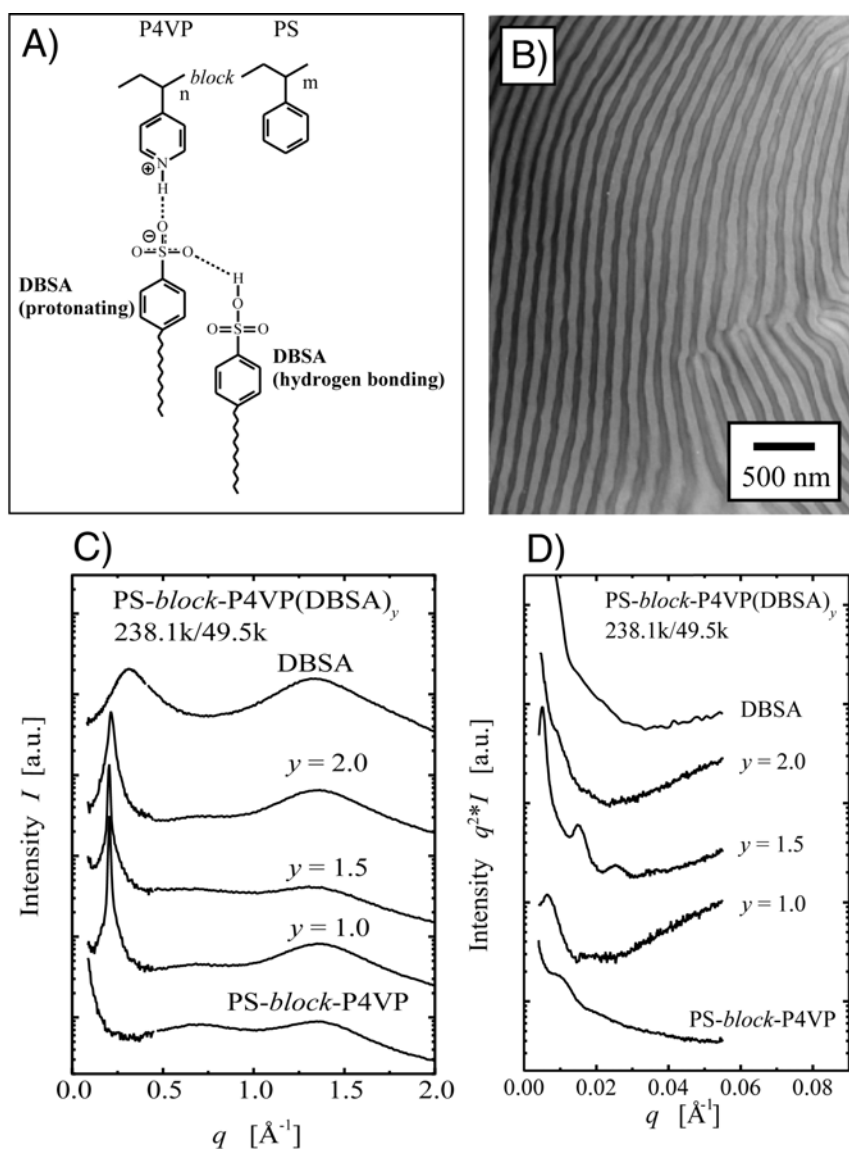


Figure 12. A) Schematic presentation of the interactions in PS-*block*-P4VP(DBSA)_y complex. B) TEM indicated that the complex PS-*block*-P4VP(DBSA)_{2.0} formed a lamellar structure with periodicity of ca. 140 nm. (TEM by J. Ruokolainen) C) SAXS curves indicated that there was smaller structure within P4VP(DBSA)_y domains ($L_p = 3.0$ nm). D) Lamellar structure with long period of ca. 130 nm was confirmed for sample PS-*block*-P4VP(DBSA)_{1.5} with SAXS.

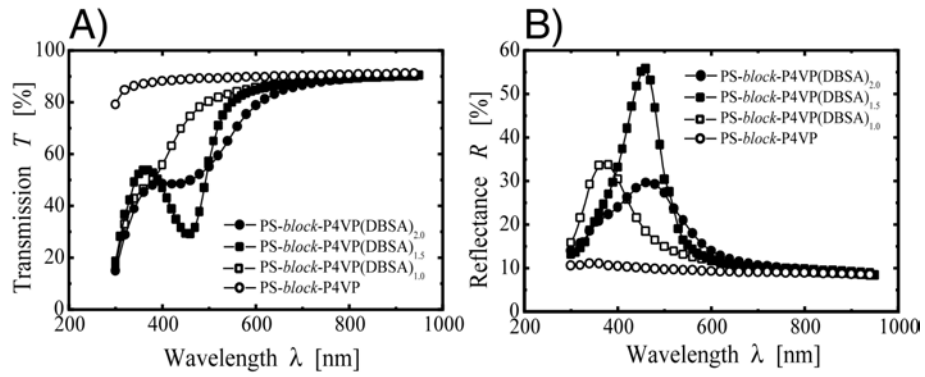


Figure 13. UV-Vis A) specular transmission and B) diffuse reflectance measurements for complexes $PS\text{-}block\text{-}P4VP(DBSA)_y$. Reflectance graphs of complexes $y = 1.0, 1.5,$ and 2.0 had the peaks at 370 nm, 460 nm, and 470 nm, respectively.

6 Conclusions

In this Thesis we examined supramolecular self-assembled nanostructures of blends of block copolymers and thermosets, polymer-amphiphile systems and structural hierarchy of block copolymer-amphiphile complexes. On the other hand, we showed that these structures can be used to modify mechanical and electrical properties of materials and that even new properties, i.e. optical functionality, which was not seen in any starting material, can appear.

Block copolymer nanostructures were used to modify mechanical properties of phenolic resins. Phenolic resin, complexed with amphiphilic diblock copolymers, P2VP-*block*-PI, formed spherical, “worm-like” cylindrical and lamellar structures. Morphology depended on the weight fraction of PI and the phase behaviour was quite similar to those expected for blends of block copolymer *A-block*-B and homopolymer A. The number of hydrogen bonds did not significantly decrease during cross-linking and there were no observable signs for the segregation between P2VP-*block* and phenolic matrix. The storage moduli at room temperature decreased slowly with increasing weight fraction of PI, when phenolic matrix was continuous. More significant decrease was observed with lamellar structure.

Structures of phenolic resin with the triblock copolymers were investigated. A spherical self-assembly with a long period of ca. 12 nm was observed when the weight fraction of PEO in block copolymer was high ($f_{\text{PEO}} = 0.40$). The tendency for macrophase separation increased with decreasing length of the PEO-blocks due to decreased number of hydrogen bonds. It is possible that wet-brush/dry-brush transition takes place in our microphase separated sample and that the growing network topologically limits the extent of the phase separation to be only local.

One-dimensional cylindrical conducting structures of nominally fully protonated PANI, where PANI chains are confined inside self-assembled cylinders, were investigated. The distance between the cylinders was ca. 3.5 nm. The conductivity of the complexes increased rapidly two orders of magnitude when the comb-shaped cylindrical structure was formed. It is probable that observed increase of conductivity is due to confinement of PANI-chains within the cylinders and due to cosolvent effects of Hres.

Molecularly reinforced polyelectrolyte with lamellar structure was demonstrated, where conductivity was decoupled from the segmental motions. P4VP and ionically conducting “liquid-like” polyelectrolyte of ethylene oxide (EO) oligomers with high segmental motions were in one lamellae and a glassy PS in another. LiClO₄ was introduced to promote

ionic conductivity. The conductivity levels were relatively low, i.e. 10^{-7} – 10^{-6} S/cm at room temperature probably due to the Coulombic traps and grain boundaries.

Finally, a high molecular weight block copolymer was complexed with amphiphiles leading to lamellar structure with long period of ca. 140 nm. All starting materials were almost colourless, but the samples were predominantly blue pearlescent in reflection to an observer viewing them in ambient. The transmission and reflectance spectra revealed the formation of an incomplete photonic bandgap at ca. 460 nm.

The results of this Thesis show that the nanostructures at different length scale can easily be obtained by combining interacting synthetic materials in solutions. These structures can lead to modified properties or even new functionalities compared to the starting materials. Future work, where concepts introduced here are used for switchable optical [174] and electrical properties [175] and selectively absorbing mesoporous materials [176], are under investigation.

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