



## Electrical switching based on dimensionality transitions in nanostructured polymers

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### Abstract

Supramolecular hierarchical conducting nanostructures are obtained by complexing amphiphilic oligomers with block copolymers. Nominally each pyridine group of poly(styrene)-*block*-poly(4-vinyl pyridine), i.e. (PS-*block*-P4VP), is first protonated by methane sulphonic acid (MSA) to yield PS-*block*-P4VP(MSA)<sub>1,0</sub>. It is further hydrogen bonded with stoichiometric amount of pentadecyl phenol (PDP) to form PS-*block*-P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub>. The polyelectrolytic domains are subject to reversible phase transitions from "semi 1d" slabs to 2d lamellae and further to 1d cylinders upon heating. The transitions manifest in the thermally activated conductivity. Extension to conjugated polymers is discussed to achieve temperature controlled switching based on electronic conductivity.

**Keywords:** self-organization in macromolecules, order-disorder phase transitions, structural phase transitions, conducting polymers, switches

### 1. Introduction

Much attention has recently been paid on solid films of electrically conducting polymers and to understand their properties in order to apply them in specific applications, for example in optical devices. Polyaniline doped by functionalized acids in combination with selected solvents allow solvent casting with high conductivity of the solid film [1]. Layer by layer deposition techniques have been developed [2], not to forget Langmuir-Blodgett concepts [3]. Thus the structure of conducting polymers can be controlled even at the nanoscale in solid films.

We aimed to explore whether it could be feasible to prepare externally controllable nanostructured electro-active polymers using another route, based on self-organization (for a recent review of self-organization in polyelectrolytes, see for example [4]). The work has been motivated by structure formation and phase transitions in block copolymers consisting of two or more mutually repulsive flexible polymers [5], block copolymers consisting of at least one rigid block (s.c. rod-coils or LC-coils) [6-9], or mesomorphic polymer-amphiphile complexes [10, 11]. In such systems, the thermodynamically equilibrium nanoscale structures are formed in bulk due to competing interactions [12]: for example in block copolymers the different blocks are mutually repulsive due to vanishing mixing entropy, leading to tendency for macroscopic phase separation. On the other hand, because the blocks are permanently, i.e., chemically connected such phase separation is

prohibited and, by contrast, s.c. microphase separation takes place [5]. Depending on the lengths of the blocks, the extent of repulsion, shear, and temperature, one may observe lamellar, cylindrical, spherical or other more advanced phases. The typical length scale of such nanostructures is 100-1000 Å. Order-disorder transitions can be observed to high temperature disordered phase and order-order transitions between the different ordered phases. Related phenomena are observed also for the LC-coil block copolymers [7, 8, 12].

The synthesis of block copolymers, and especially LC-coil block copolymers, may be difficult. This fact encouraged us to search for alternative routes to prepare materials that behave as blocks copolymers and would have analogical nanostructures, phase behavior and flow properties [13-16] but which would be more straightforward to "synthesize". One answer turned out to be the observation that "block copolymer-like" materials can be constructed using a supramolecular route [17] where the permanent chemical bonding is replaced by suitable physical attractive interaction, such as hydrogen bonding, coordination complexation [18], charge transfer [10] or their sterically tailored combination, i.e. molecular recognition (to illustrate how to combine hydrogen bondings and  $\pi$ -stackings in context of conducting polymers, see [19]).

A model polymer was selected to be poly(4-vinyl pyridine), i.e. P4VP,  $-\text{CH}_2-\text{CH}(\text{C}_5\text{H}_4\text{N})-$  (see also Fig. 1), due to its chemical similarity with selected nitrogen containing conducting polymers, notably polyaniline (PANI):

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1) PANI can be doped for conductivity by strong acids, such as sulphonic acids, due to proton transfer [20]. Analogical reaction takes place also for the pyridine group of P4VP to form a charged pyridinium ring. At this point we emphasize that electronic conductivity is thus not obtained in the case of P4VP but the prior literature suggests that ionic conductivity could still be possible (for poly(ethylene imine) complexed with sulphuric acid, see [21]).

2) In the case of PANI, it has turned out that, in combination with especially camphor sulphonic acid, phenolic solvents yield high solubility [1], for which an explanation has been suggested based on molecular recognition [22]. The phenolic compounds are particularly fascinating also in combination with P4VP, even without the protonating acids, because strong hydrogen bonding takes place between the (acidic) phenolic hydroxyl group and the (basic) pyridine group. This allows to hydrogen bond nominally one amphiphilic alkyl phenol molecule  $C_nH_{2n+1}-C_6H_4-OH$ , such as pentadecyl phenol (PDP,  $n=15$ ) or nonadecyl phenol (NDP,  $n=19$ ), to each pyridine group to form polymer complex that has an architecture resembling comb-block copolymers. In this case the repulsive interaction takes place between the nonpolar alkyl tails (combs) of the alkyl phenols and the polar polymer backbone whereas the hydrogen bonds prevent the combs from phase separation. Such complexes form lamellar nanostructures at the length scale of ca. 40 Å near room temperature [11, 13, 14, 16]. Heating causes order-disorder transition where the nanoscale order is lost but the order is reversibly recovered upon recooling. We point out that this transition is not related to breaking of hydrogen bonds, as order-disorder transition can also be observed in selected block copolymers. Thus polymer/amphiphile complexes allow formation another mesomorphic order at the length scale of ca. 20-50 Å, strongly resembling block copolymeric behavior.

In this work such two levels of structure have been combined within a single material which has, in addition, been protonated with sulphonic acid. Thus a model compound is obtained that allows to study hierarchical nanostructures using materials which are experimentally amenable but which are still sufficiently near to the corresponding conducting polymers (such as PANI) to obtain predictions for their behavior. In addition, we study whether order-disorder and order-order transitions within self-organized polymers could offer a concept for switching. For another route for electrical switching based on thermoreversible gels of PANI, see [23].

## 2. Experimental

To provide the “long length scale”, a diblock copolymer consisting of polystyrene (PS) block of length 40000 daltons and P4VP-block of length 5600 daltons (PS-*block*-P4VP) was selected with a narrow polydispersity 1.09 (Polymer Source Inc.). PS-*block*-P4VP was dissolved in chloroform and nominally one methane sulphonic acid molecule (MSA) and pentadecyl phenol molecule (PDP) was added for each pyridine group. The sample was stirred at mild heating and finally chloroform was evaporated. After vacuum drying at 60 °C for 4 days, the material was stored in a desiccator. The expected structure, denoted as PS-*block*-P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub>, is shown in Fig. 1. That the protonation had indeed taken place was checked using FTIR [24]. That the hydrogen bonding between the phenolic hydroxyl and sulphonate group takes place, has to be inferred indirectly due to the large width of the corresponding

FTIR absorption. Thus an architecture is formed that consists of diblock copolymer where the P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> block forms a comb-like structure, the PS block forms a coil, and thus can be called as comb-coil diblock copolymer. The short length scale ordering is expected to form as an internal structure within the comb-like block, see the scheme of Fig. 2.

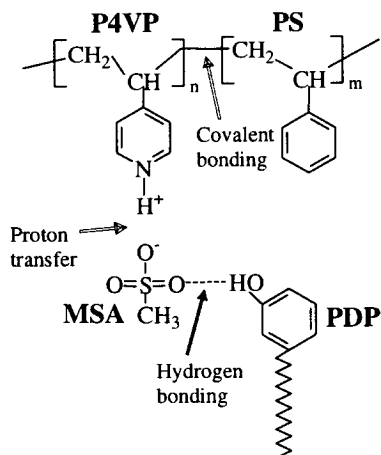


Fig. 1. The expected bondings within PS-*block*-P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub>.

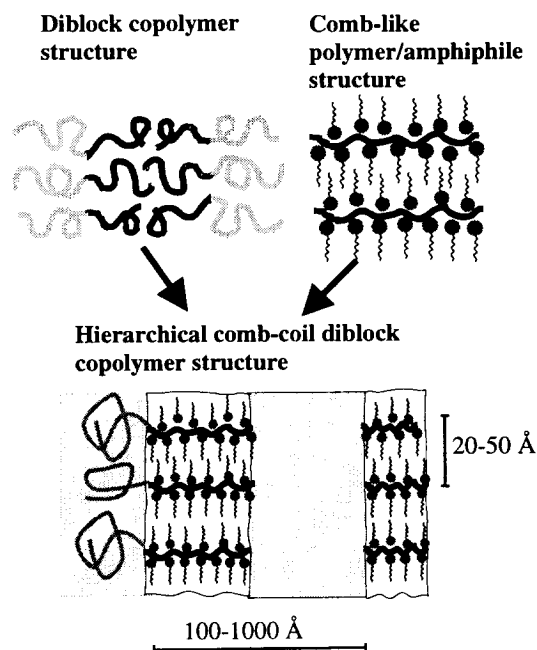


Fig. 2. Schematics to combine the block copolymer length scale and polymer-amphiphile length scale to a single comb-coil diblock copolymer to form hierarchical nanostructures (in this case lamellar-*within*-lamellar structure).

## 3. Results and discussion

Small angle X-ray scattering (SAXS) in combination with transmission electron microscopy (TEM) allows a means to investigate whether structures such as shown in Fig. 2 indeed

form. For SAXS intensity patterns as a function of temperature, see Fig. 3 [24]. Near room temperature, a SAXS intensity maximum is observed at the magnitude of the scattering vector  $q_2=0.017 \text{ \AA}^{-1}$ . A second order peak becomes distinct at  $2q_2$  upon slight heating, possibly because the PS domains become softened near the glass transition temperature. Therefore, one can conclude that the PS and P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> blocks form alternating lamellar domains at the periodicity of  $350 \text{ \AA}$  [24]. In addition, another intensity maximum is observed at  $q_1=0.13 \text{ \AA}^{-1}$ . Higher order peaks are not resolvable in this case. However, based on experience on P4VP-PDP complexes (i.e. without MSA) where the second order peak is observed at twice of the main intensity maximum [13] and on P4VP-NPD where the lamellar order is directly resolved using TEM [14], it is suggested that the intensity maximum at  $q_1$  is due to lamellar order even in this case. The long period of this shorter length scale is  $48 \text{ \AA}$ . A scheme for the hierarchical structure is shown in Fig. 4a, illustrating that the P4VP(MSA)<sub>1,0</sub> domains are of the form of "semi 1d" nanoscale slabs. Direct TEM image of the structure is not so far available. However, the TEM micrographs for a closely related material consisting of PS-*block*-P4VP(NPD)<sub>1,0</sub> confirm such hierarchical structures [24].

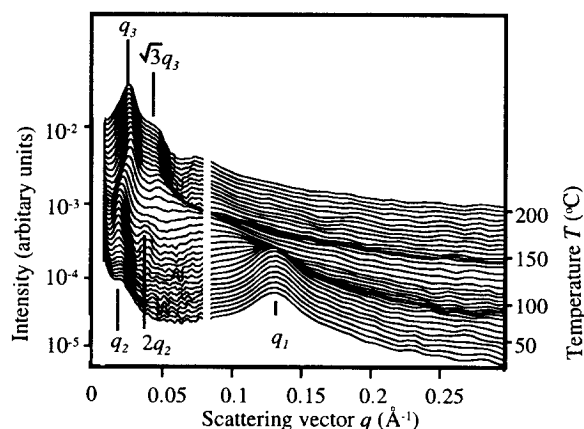


Fig. 3. Small angle X-ray intensity patterns at different temperatures for PS-*block*-P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> [24].

A change in the SAXS scattering data is observed at  $100^\circ\text{C}$ , above which the intensity maximum at  $q_1$  is not observed. Similar SAXS behavior takes place also in the homopolymer P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> where additionally birefringence is lost in polarized optical microscopy upon heating past the same temperature [24]. This transition can be assigned to order-disorder transition temperature above which the lamellar order at the shorter length scale within the P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> lamellae does not take place. Notably, the longer length scale (block copolymer) lamellar order still occurs. The resulting structure is depicted in Fig. 4b.

Further increase of temperature past ca.  $150^\circ\text{C}$  yields another transition: In this case the longer length scale shows the scattering intensity maxima at  $q_3=0.028 \text{ \AA}^{-1}$  and at  $\sqrt{3}q_3$ , indicating an order-order transition to a hexagonal order, see Fig. 4c. Such transition is due to two reasons: firstly, PDP macroscopically phase separates from P4VP(MSA)<sub>1,0</sub> at a high temperature range [24] and secondly PDP becomes miscible with PS and therefore, the effective volume fraction of the block containing P4VP(MSA)<sub>1,0</sub> is reduced.

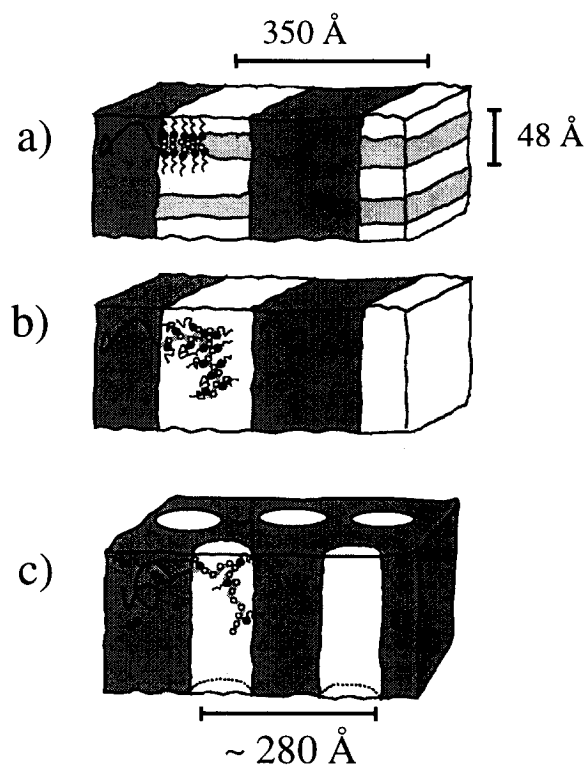


Fig. 4. Schematic illustrations of the structures of PS-*block*-P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> at different temperatures. a) Lamellar-*within*-lamellar hierarchical structure observed between room temperature and ca.  $100^\circ\text{C}$ . In this case P4VP(MSA)<sub>1,0</sub> forms "semi 1d" slabs; b) For  $100^\circ\text{C} < T < 150^\circ\text{C}$  the P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> lamellae have disordered internal structure. Therefore P4VP(MSA)<sub>1,0</sub> is confined in 2d sheets; c) For  $T > 150^\circ\text{C}$  a hexagonal order is observed in which case P4VP(MSA)<sub>1,0</sub> is confined in 1d cylinders. For clarity, only one chain has been plotted.

Let us finally study the conductivity behavior using HP4192LF Impedance Analyzer at the frequency range 10Hz-10 MHz. A separate study of homopolymeric P4VP(MSA)<sub>1,0</sub> shows classical thermally activated conduction, suggesting protonic conduction [24]. For example at  $160^\circ\text{C}$  the ionic conductivity is of the order  $10^{-4} \text{ S/cm}$ . Embedded in the block copolymer PS-*block*-P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub>, an interesting behavior is observed. At low temperature where P4VP(MSA)<sub>1,0</sub> forms the nearly 1d slab geometry (see Fig. 4a) the conductivity is very low, in the range  $10^{-8}$ - $10^{-7} \text{ S/cm}$ , see Fig. 5. Upon heating an increase in the conductivity takes place at  $100^\circ\text{C}$  which coincides with the internal order-disorder transition within the P4VP(MSA)<sub>1,0</sub>(PDP)<sub>1,0</sub> lamellae. It is natural to assign such behavior with the dimensionality transition, shown in Fig. 4. Further increase of temperature causes a reduction of the conductivity near the transition where the hexagonal order takes over. It is tempting to assign the reduction of the conductivity to the transition to 1d conductive pathways.

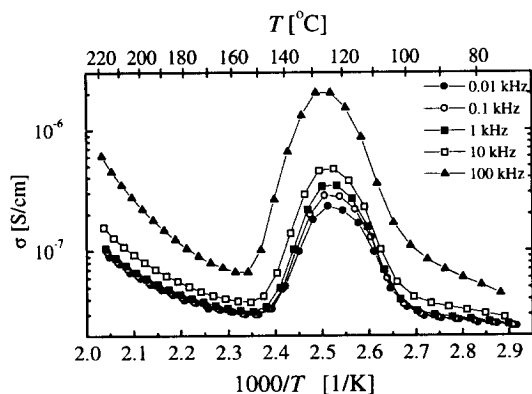


Fig. 5. AC impedance of PS-*block*-P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub> at different frequencies during heating.

The SAXS intensity patterns are reasonably reversible both upon heating and cooling. Reversibility is observed also in the conductivity (see Fig. 6) especially taken into account that in this shown case the sample has been heated to the quite high temperature of 220°C.

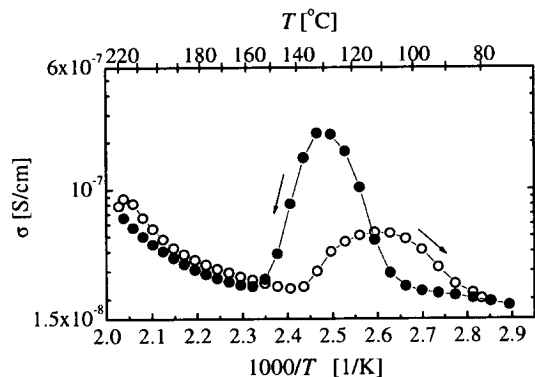


Fig. 6. AC conductivity at 1 kHz for PS-*block*-P4VP(MSA)<sub>1.0</sub>(PDP)<sub>1.0</sub> upon heating and cooling.

Finally some concluding remarks can be made. Supramolecular concepts allow comb-coil diblock copolymer architectures that provide nanoscale order at two length scales. Therefore, selected controlled nanoscale "shapes" of conducting pathways of different dimensionalities can be constructed. The concurrent phase transitions allow switching of electrical signal by controlling by temperature. The modulation in the conductivity in the present studies was still limited. However, it seems to us that the switching ratio could be increased by orientating the nanostructures for example by shear. Such work is now in progress. It seems promising to transfer the concepts next to polymers that have conjugated blocks to study switching of electronic conductivity.

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